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MERCURY CONTROL FOR MWCs USING THE SODIUM TETRASULFIDE PROCESS

by
Anthony Licata
Babcock Borsig Power, Inc.
Worcester, MA
and
Dr. Wolfgang Schüttenhelm
BBP Environment GmbH
and
Dr. Marton Klein
BBP Environment GmbH
Gummersbach, Germany

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BABCOCK BORSIG POWER

Babcock Borsig Power, Inc.
Post Office Box 15040
Worcester, MA 01615-0040
www.bbpwr.com

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ABSTRACT

When choosing among various technologies for mercury control for flue gases of Municipal Waste Combustors (MWCs) not only ecological but also economical criteria are decisive in restricting waste processing costs to a justifiable rate. The use of additives provides a significant potential, especially for plants already equipped with a spray dryer/bag house system for achieving compliance at relatively low cost.

The use of sodium tetrasulfide (Na2S4) as an additive for the inexpensive control of mercury emissions is presented as a possibility to combine both ecology and economy. Particularly with the new requirements in the U.S., this technology offers the opportunity to bring most MWCs into compliance with respect to their Hg emissions.

This paper focuses on the German requirement for mercury monitoring and the most recent applications of this process installed on several European MWCs, hazardous waste incinerators, and sewage sludge combustors. Pilot plant tests on a MWC showing the control potential of the Na2S4 process is also presented.

INTRODUCTION

Reducing Hg emissions has become a primary goal of environmental regulators around the world. In 1986, Germany became one of the first countries to regulate Hg emissions from their waste-to-energy plants (WTEs). These Hg regulations were soon adopted by other western European nations and then by the European Community (EC). The U.S. EPA began formulating a Hg emission standard for MWCs in the late 1980s. Several states also began setting Hg emission standards for MWCs, some of which are more restrictive than the EPA's.

The original German Hg standard was 50 µg/Nm^3 at 11% O2 which is equal to 65 µg/dscm at 7% O_2. EPA set the Hg emission limit for MWCs at 80 µg/dscm at 7% O_2, or 85% reduction, which ever is less restrictive. Although it does not appear to be a significant difference between these two standards, the German standard does not provide a provision for a percent reduction that may make it significantly more restrictive than U.S. standards. In February 1999, Germany reduced the Hg emission standard for MWCs to a daily average of 30 µg/Nm^3 at 11% O2 using CEMS.

Several U.S. states have proposed or adopted a Hg emission standard of 28 µg/dscm at 7% O_2 or 85% reduction which ever is less restrictive. The Commonwealth of Massachusetts has proposed a standard of 28 µg/dscm at 7% O_2 without a percent reduction. To date, most MWCs in the U.S. have used several different activated carbon adsorption technologies with spray dryers and either ESPs or fabric filters to control Hg emissions. These new proposed regulations have raised concerns with the owners and operators of MWCs for the following reasons:

- There is very little long-term operating data on Hg emissions control using activated carbon adsorption to maintain continuous compliance at 28 µg/dscm.
- German MWCs have operating experience at this emission level using different air pollution control technologies in multiple stages and having different economic impacts.
- It will require using significantly more activated carbon in order to operate at the lower Hg levels. This raises additional questions. What impact will this additional activated carbon have on plant operations? What will the cost of activated carbon be in the future as demand increases? Will sufficient amounts of activated carbon be available?
- Will MWCs equipped with a spray dryer and ESP be able to meet these new standards?

L. & C. Steinmüller GmbH, now part of BBP Environment GmbH, developed a new technology - sodium tetrasulfide (Na_2S_4) - that addresses these issues. This technology should not be confused with sodium sulfide Na_2S that was tried in both Europe and the U.S. without success. The shortcomings of Na_2S are that it can leave a strong odor of hydrogen sulfide (H_2S) in the MWC ash and it does not control all species of Hg. The major advantages of the Na_2S_4 technology are that it controls elemental as well as ionic forms of Hg, and due to dissociation in the flue gas, H_2S under normal operating conditions is not a problem.

Other advantages of the Na_2S_4 technology are:

- The reaction yields stable inert reaction products.
- Na_2S_4 is a liquid and is easier and safer to handle than powered activated carbon. Also, being a liquid, the feeding and control of Na_2S_4 is simpler and more positive than powdered activated carbon.
- The higher ratio of elemental Hg fraction produced in industrial/hazardous waste incinerators, sewage sludge incinerators, and coal-fired power plants is easier to control with Na_2S_4 than with powdered activated carbon.
- Additive consumption is easy to optimize and is not dependent on a build-up in the filter cake.
- Activated carbon is abrasive and results in higher maintenance cost due to replacement of conveying pipes and rotary equipment.

At higher temperatures, mercury compounds are not very thermally stable, therefore, the mercury is gaseous at a temperature of 850°C (1562°F) in the combustion chamber, independent of the kind of compound that is taken into the refuse combustion plant. The minimal retention of mercury in the slag is due to its high vapor pressure and is less than 5% of the total mercury input as shown in various investigations. Other metals such as copper, chromium, or nickel have a slag retention rate of more than 90%.

The mercury vapor from the combustion process reacts and mixes with the flue gas and enters the convective section, which is an integral part of the boiler. Due to the decreasing gas temperature, the elemental mercury is able to react with other flue gas components.

The main reaction of the mercury vapor is the formation of mercury (II) chloride (HgCl2) out of the gaseous hydrochloric acid (HCl) and elemental mercury (Hg0) under oxidizing conditions of the off-gases downstream of the waste combustor. The exact mechanism of this reduction reaction has not yet been completely understood but is usually described as follows:

$$\mathrm{Hg0} + 2\,\mathrm{HCl} \Leftrightarrow \mathrm{HgCl_2} + \mathrm{H_2O} \qquad \text{(Eq. 1)}$$

In case of decreasing temperature, the equilibrium of this reaction shifts more and more to the right side. However, the reaction is not only dependent on temperature. Other flue gas components such as O_2, sulfur compounds and HCl as well as the residence time in a certain temperature range, influence the reaction equilibrium.

The thermodynamic balance of the above mentioned reaction appears to be blocked kinetically. Therefore, a complete transformation of the Hgo into HgCl2 cannot be expected. The mercury chloride thus formed has a high volatility and is found in the gas phase in the boiler (see Table I).

Table I Selected physical properties of Hg and Hg compounds

	Mercury (Hg^0)	Calomel (Hg_2Cl_2)	Sublimate ($HgCl_2$)	'Meta-Cinnabarite' (black, meta-stable) 'Cinnabar' (red, stable) (HgS)	Mercury-oxide (HgO)	Sulfur (S)	Sodium tetra-sulfide (Na_2S_4)
Melting temperature (°C) at p = 1 atm.	-38.84	Solid	280	Solid	Solid	118.95	275
Boiling temperature (°C) at p = 1 atm.	356.95		303			444.6	
Sublimation temperature (°C) at p = 1 atm.		383		580			
Vapor pressure at p = 1 atm., 20°C	0.0017 mbar =15,000 µg/m^3						
Formation/ Decomposition				Decomposition, oxidizing atmosphere & ≥ 400°C	Formation 300-350 °C Decomposition > 400 °C		

In addition to the formation of mercury (II) chloride, other reduction reactions of mercury in the gaseous phase are possible:

- Elemental mercury can be oxidized to mercury(I) chloride (Hg_2Cl_2):

$$2\,Hg0 + 2\,HCl + \frac{1}{2}\,O_2 \Leftrightarrow Hg_2Cl_2 + H_2O \qquad \text{(Eq. 2)}$$

- Elemental mercury can be oxidized to mercury oxide (Hg0):

$$2Hg^0 + O_2 \Leftrightarrow 2\,Hg0 \qquad \text{(Eq. 3)}$$

However, at more elevated temperatures, the above described reaction possibilities (Eq. 2 and Eq. 3) are of less importance as Hg_2Cl_2, and Hg0 are not stable at temperatures above 400°C (752°F). Above this temperature, Hg_2Cl_2 decomposes into Hg0 and $HgCl_2$ respectively and Hg^0 into Hg0 + ½ O_2.

A higher amount of mercury (I) chloride can be formed out of HgCl2 in the presence of fly ash creating a reducing atmosphere. At the boiler's outlet temperature the Hg2Cl2 is solid and will be separated together with the fly ash (sublimation temperature 383°C (721°F), see Table I). Consequently, up to 10% of the total mercury amount can be removed.

In the case of municipal solid waste combustion, the mercury at the boiler outlet consists mainly of 5 to 15% as Hg^0 and 85 to 95% as $HgCl_2$. The elemental mercury portion can increase drastically in two ways:

1. as the amount of SO_2 exceeds the amount of HCl by an order of magnitude, or
2. if there is no residence time for the $HgCl_2$ formation due to simple quenching.

The portion of elemental mercury in the flue gas originating from a sewage sludge incinerator or a coal-fired power station is usually about 30 - 40% as Hg^0. A characteristic of both Hg^0 and $HgCl_2$ is their high vapor pressure, even at temperatures as low as 200°C (392°F). Accordingly, since a large portion of the mercury species is in the vapor phase, the particulate removal equipment, which is usually arranged downstream of the boiler, is unable to act as an effective mercury sink.

MEASURES FOR MERCURY CONTROL

In addition to the Hg-separation via Na_2S_4 as presented in this paper, there are other processes for the Hg minimization in flue gas. Of course $HgCl_2$ can be successfully separated in wet scrubbers and, to some extent, in spray absorbers of a flue gas cleaning system as well. The disadvantage is that this equipment is ineffective in trapping metallic mercury.

Metallic and ionic mercury can both be captured in special filters. The activated carbon fixed-bed filter is the tried and safest possibility to separate both forms of mercury down to the detection limit. Furthermore, activated carbon can also be injected into the flue gas duct. Usually, in these so-called entrained flow processes, spent activated carbon is again removed by means of a downstream fabric filter.

Alternative processes, especially for the separation of elemental mercury, have been proposed recently, e.g., the application of zeolite in the so-called medisorbon process or the amalgamation on precious metals. However, all such filtration processes share the fundamental disadvantage of involving a separate apparatus in the flue gas path. In addition, the disposal of the spent, heavily contaminated sorbent frequently presents severe problems. The high investment and operating costs for the filters must call the economy of such a system into question.

The Na_2S_4 Process for Mercury Separation

The disadvantages of the various conventional processes as described above forced Steinmhüller/BBP Environment to develop its own principle of mercury separation using Na_2S_4 which can capture both ionic $HgCl_2$ and Hg^0 in accordance with the following simplified reactions:

$$Na_2S_4 + HgCl_2 \Leftrightarrow HgS + 2NaCl + 3\,S^0 \qquad \text{(Eq. 4)}$$

$$S^0 + Hg^0 \Leftrightarrow HgS \qquad \text{(Eq. 5)}$$

It is sufficient to inject an aqueous Na_2S_4 solution into the flue gas duct and such a system can be easily retrofitted to an existing flue gas cleaning plant. The Na_2S_4 reacts with the mercury to form mercury sulfide (HgS) whose red allotrope is known as cinnabar. This is a non-poisonous insoluble salt that is thermally stable up to 400°C (see Table I) and thus, effectively immobilizes the mercury by chemical binding. The black allotrope known as meta-cinnabarite, found in waste combustion facilities, changes into the stable red allotrope in the course of several years,

Apart from the heat exchange with the flue gas, there is also a mass transfer between the droplet of the additive and the flue gas. The most likely mass transfer process between the liquid and the gaseous phase is the dissolving of HCl in the droplets of the Na_2S_4 as aqueous alkaline liquids show a strong affinity towards the gaseous HCl.

The dissolved HCl will decompose the existing Na_2S_4 in the droplets as follows:

$$Na_2S_4 + 2\,HCl \Leftrightarrow H_2S + 3\,S + 2\,NaCl \qquad \text{(Eq. 6)}$$

After evaporation of the droplet, the H_2S injected into the flue gas is gaseous at a temperature of approximately 220°C (428°F). Elemental sulfur is then formed (melting point of sulfur = 119°C (246°F), boiling point = 445°C (833°F)) (see Table I) and exists in liquid form as an aerosol with a diameter of < 1 µm.

However, it is most unlikely that the HCl will decompose all Na_2S_4 molecules. Because Na_2S_4 (melting point = 275°C) is stable at the existing temperatures, it is most probable that Na_2S_4 particles can still be found in the flue gas after evaporation of the droplet.

In the entrained-flow phase, the mercury reacts with $H_2S^{(g)}$, $S^{0\,(1)}$, and Na_2S_4. According to the predominant opinion in literature and also according to the steam pressure curve for pure components, Hg^0 and $HgCl_2$ can be found in the gaseous phase due to their high volatility. However, the existence of aerosols cannot be denied. Therefore, different reaction mechanisms must be responsible for the formation of HgS within the entrained-flow phase. It is most probable that Hg^0 and $HgCl_2$ are dissolved in the droplet of the additive where they react as follows:

$$HgCl_2 + H_2S \Leftrightarrow HgS + 2\,HCl \qquad \text{(Eq. 7)}$$

$$Hg^0 + S^0 \Leftrightarrow HgS \qquad \text{(Eq. 8)}$$

These reactions are not only dependent on the distribution of educts but also on the time-limited existence of a liquid phase. Other reaction schemes exist (melting temperature Hg^0 and $HgCl_2$: - 40°C and 280°C, boiling temperature: 360°C and 303°C) (see Table l) to account for the presence of Hg^0 and $HgCl_2$ as aerosols.

Hg0 and HgCl2 Aerosols

Hg0 and HgCl2 aerosols respectively, can be combined with Na2S4 particles, and can be absorbed and react as follows:

$$\mathrm{HgCl2 + Na2S4 \Leftrightarrow HgS + 2\,NaCl + 3\,S^0} \qquad \text{(Eq. 9)}$$

$$\mathrm{Hg^0 + Na2S4 \Leftrightarrow HgS + Na2S3} \qquad \text{(Eq. 10)}$$

According to Eq. 7, H2S$^{(g)}$ can react to form HgS in the gaseous phase as well as in the liquid phase with the HgCl2 aerosols. S$^{0,(l)}$ can also be combined with Hg$^{0,(g)}$ and Hg^0 aerosols and react to form HgS as mentioned in Eq. 8.

Competitive reactions such as the oxidization of Na2S4, H2S or S into Na2SO3, SO2, SO3, or S2O3 cannot be excluded. Such competitive reactions would prevent the sulfur from further reactions with mercury. Moreover, sulfide formation of other heavy metals can cause competitive reactions as well. However, in the case of injection after upstream dust removal, such reactions are of no consequence regarding the sulfur balance. Even if all heavy metals in the flue gas flow react to sulfides, only 4-10% of the sulfur fed could be used up via the Na2S4 injection.

Finally, the equations Eq. 7 and Eq. 8 have to be indicated as the basic reaction equations responsible for the transformation of Hg^0 and HgCl2 during the entrained-flow phase that is started by the reaction of Na2S4 with dissolved HCl (see Table II).

Table II Results of trial run with Na2S4 injection

Kassel Waste -to-Energy Plant, November 1995 L. & C. Steinmüller GmbH													
	Raw Gas					Clean Gas					Removal Efficiency (%)		
	Content (μ/m^3_N)			Distribution (%)		Content ($\mu g/Nm^3$)			Distribution (%)				
No.	Hg_{ges}	Hg^0	Hg^{2+}	Hg^0	Hg^{2+}	Hg_{ges}	Hg^0	Hg^{2+}	Hg^0	Hg^{2+}	Hg_{ges}	Hg^0	Hg^{2+}
1	78	24	54	31	79	16	2	14	12	88	79.5	92	74
2	73	28	45	38	62	27	4	23	15	85	63	86	49
3	57	19	38	33	67	20	1	19	5	95	65	95	50
4	212	58	154	27	73	36	1	35	3	97	83	98	77
5	138	22	116	16	84	46	4	42	9	91	67	82	64
6	101	11	90	11	89	53	2	51	4	96	47.5	82	43
7	138	20	118	14	86	47	3	44	6	94	66	85	63
8	57	28	29	49	51	25	1	24	4	96	56	96	17
Mean	107	29	81	27.5	72.5	34	2	32	7	93	66	89	55

OPERATION EXPERIENCE WITH NA2S4

The Peel Resource Recovery Project in Brampton, Ontario is currently undergoing a retrofit that includes the installation of a Na2S4 system for Hg control. In addition, six plants have already been built or are under construction in Europe that also include the Na2S4 system for Hg control (see Table III). The most recent project is described in the following section.

Table III Flue gas cleaning systems with Na2S4

Plant	Kassel MHKW	Gevudo Dordrecht NL	VERA Hamburg	RVA Boehlen
Fuel	MSW & commercial waste	MSW	Sewage sludge	Hazardous waste
Capacity/ Flue gas flow rate	2 x 10 t/hr 2 x 65,000 m^3/hr (wet)	4 x 7.5 t/hr 2 x 130,000 m^3/hr (wet)	2 x 3 t/hr. (dry solids) 2 x 21,200 m^3/hr (wet)/3 lines	1 x 3.33 t/hr 1 x 30,000 m^3/hr (wet)
Na$_2$S$_4$ Purpose	• Hg sink • Hg immobilization	• Minimization of coke addition upstream of entrained flow FF • Hg immobilization	• Hg sink • Preliminary Hg capture for producing high quality gypsum	
Hg in uncontrolled flue gas (mg/Nm^3)	0.2 – 0.6	0.7	1.35	6.0
Start-up	March 1997	Nov. 1996	Dec. 1996	Sept. 1997

Peel Resource Recovery

A municipal waste-to-energy (WTE) facility located near Toronto, Canada has been in operation since 1992. The facility was constructed with a state-of-the-art air pollution control system (APC) designed to meet emission standards that include < 20 mg/Rm3 @ 11% O2 particulate emissions and 0.5 ng TEQ/Rm3 @ 11% O2 PCDD/PCDF. The facility has operated at an average 91% availability since start-up and consistently met the emission standards during annual and semi-annual testing.

The owners of the facility recognized the need to expand the facility capacity by 20% by installing a new combustor. However, by installing this new capacity, the facility became subject to new air pollution limits. During deliberations on the expansion, several alternatives were considered. It was concluded that adding to the existing combustion equipment and upgrading the APC system through add-on technology offered the most cost-effective means of providing additional disposal capacity at the facility.

A conventional flat tipping floor inside a pre-fabricated steel building forms the basis of the waste receiving and handling system. Waste from the floor is fed to a National Recovery Technology fuel enhancement system (NRT) that homogenizes the waste while removing glass, fines, and a limited amount of metal before a series of conveyors return it to the storage area. Front-end loaders are used to charge the furnaces. There are four Consumat 110 metric ton tonne)/day (100 tons/day) furnaces each with dedicated heat recovery boilers. The flue gases from the 4-furnace/boiler systems are collected in a common duct leading to the APC system. The APC system consists of two parallel APC trains, which include:

- A wet spray humidifier or evaporative cooling tower (ECT) where water is injected and the gases are cooled,
- A venturi reactor or dry scrubber (DS) where powdered lime is added to remove acid gases, and
- A fabric filter (FF) where the particulate matter is removed from the gas stream.

Each APC train discharges through an induced draft (ID) fan into a single flue stack. Each of the existing APC trains had been designed to accommodate the flue gases from three operating furnaces. The system was approved to operate in this mode and was tested while operating in this mode on several occasions during the first two years of operation. No statistically significant changes in emission concentrations were found when the test data were examined suggesting that no changes were required to incorporate the 5th furnace into the existing system. However, with more stringent emission limitations additions were required on the APC system.

When the regulators rescinded a ban on WTE facilities introduced in the early 1990s, they tightened air emission standards for new facilities to the equivalent of the U.S. EPA large facility standards promulgated in 1995. Existing facilities, such as the one in question, were exempt from tighter controls provided no changes were made in the facility. Expanding the capacity, however, triggered the need to comply with the tighter standards. The new guideline lowered allowable emissions for PCDD/PCDF, particulate matter, HCl, and SO_2, and imposed new emission limitations for mercury, cadmium, lead and NO_x. The present APC system meets all the new emission limitations with the exception of the ones for PCDD/PCDF, mercury and NO_x while operating in the high flow mode. Thus the owners needed to find control measures that would be suitable for reducing mercury, PCDD/PCDF and NO_x emissions to the newly required levels if the facility was to be expanded.

While several alternative measures were available as add-ons to the existing system to control mercury and PCDD/PCDF emissions, the biggest technical challenge was to find a reasonably priced system to reduce NO_x emissions. This had to be accomplished within the constraints offered by the existing furnace configuration and the required emission limitations.

The project details were presented inwas detailed in the paper "Retrofit of a WTE with SCR for NO_x and PCDD/F Control and Na_2S_4 Injection for Mercury Control," presented at the 1999 NAWTEC conference.

The project team decided that the most economical and practical approach was to install an SCR to control NO_x and dioxins and to install a Na_2S_4 system for Hg control in order to meet a mercury emission limit of 50 $\mu g/Rm^3$ at 11% O_2 (65μg/dscm at 7% O_2) with no percent reduction provision.

The Na_2S_4 system consists of a mixing and dosing station and a lance to inject the Na_2S_4 solution into the ductwork. The Na_2S_4 is purchased in a 34% to 40% concentrated solution in 55 gallon barrels or 1 m^3 containers. In the mixing station, the Na_2S_4 solution is diluted to 5% with deionized water and then pumped proportionally to the injection lance. A typical process flow sheet is shown in Figure 1. The mixing station in housed in a 6 x 2.5 meter (20 x 8 foot) prefabricated building. This building with all of the pumps, meters and programmable logic controls (PLC) will be delivered to the site as a complete package. The only installation will be the heat-traced pipes from the mixing station to the injection lance, the installation of the injection lance in the flue duct, and the connection of the DI water, potable water, and electrical interconnections from the plant to the mixing station. The start-up of the retrofit is scheduled for June 2000.

Avedøre Sewage Sludge Combustor

At the Avedøre power station site, located near Copenhagen, Denmark, a new sewage sludge combustor is under construction and will be commissioned this summer. The Avedøre sewage sludge combustion plant is designed to dispose of a portion of the sludge produced in the city of Copenhagen's sewage works. Combustion and flue gas cleaning take place in one line burning about 1.5-t/h sludge (dry substance) and generating 14,000 m^3/h (STP, wet) (8,877 scfm) flue gas.

After combustion, the flue gases pass through the boiler and an electrostatic precipitator in which the greater part of the fly ash is removed at a temperature of approximately

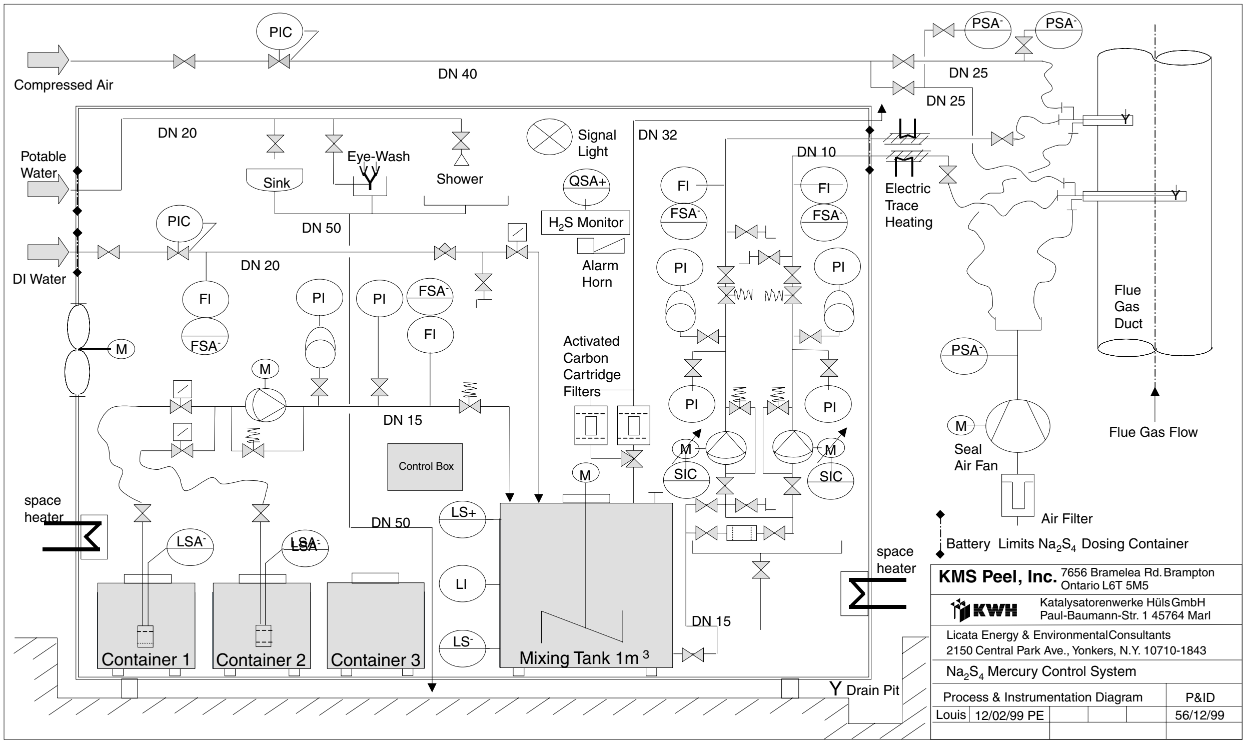

Figure 1 Process diagram, Peel Project

220°C. The fly ash will be utilized as a building material. Downstream of the electrostatic precipitator an economizer section recovers a part of the flue gas heat to increase the boiler feed water temperature. The flue gas temperature downstream of this economizer is about 160°C (320°F).

After cooling the flue gas in the economizer, Na2S4 is injected into the gas flow upstream of a fabric filter. A sodium tetrasulfide concentrate of 40% is diluted to a 5% solution with softened water. The diluted solution is atomized into the flue gas by means of compressed air. In addition, hydrated lime and activated carbon are injected into the gas stream to control dioxins. The Na2S4 process being supplied by BBP Environment provides the elemental mercury and ionic mercury capture. Ionic mercury will also be adsorbed on the activated carbon and the last traces of this mercury species will be separated in the subsequent hydrochloric acid scrubber. Elemental mercury cannot be controlled by means of a wet scrubbing system. The bleed from the HCl scrubber is subjected to physical and chemical effluent processing before being discharged.

The following SO2 scrubber takes up the sulfur dioxide contained in the flue gas. In order to minimize an off-gas plume at the stack, the saturated flue gas from the scrubbers passes through a steam re-heater which is designed for an outlet temperature of 130°C (266°F).

The Na2S4 process was selected due to the high mercury inlet concentration of 1.1 mg/Nm^3 @ 11% O2 (design value) which has to be controlled to below 50 µg/ Nm^3 @ 11% O2). Since the concentration of HCl in comparison with SO2 is very low, a large fraction of elemental mercury is expected which has to be reduced by at least 90% by means of Na2S4 in order to meet the total mercury stack emission limit. The ionic mercury control efficiency of the Na2S4 process is guaranteed to at least 80%. Activated carbon addition on its own is not expected to be sufficient to meet this goal.

Pilot Plant Test Program

There was considerable concern regarding the economics and viability of activated carbon injection technologies to meet the proposed Massachusetts mercury standard of 28 µg/dscm with no reduction exclusion on a long-term basis especially on MWCs equipped with a spray dryer and ESP. Since the principal advantage of the Na2S4 technology is that it is more effective in controlling both elemental mercury (Hg^0) and ionic mercury (Hg^{2+}) than activated carbon, BBP Environment wanted to determine if the Na2S4 technology would be applicable. Na2S4 has been demonstrated to reduce Hg emissions in several European plants to the new proposed standard, however, there was no experience with the application of this technology to U.S. facilities. In 1998 BBP Environment undertook a test program on a pilot plant MWC equipped with a spray dryer and ESP to determine the following:

- Could Na2S4 meet the new proposed emission standard on a short-term operating period?
- Would there be an advantage to using activated carbon injection and Na2S4 in combination to meet the proposed Hg emission standard on a short-term operating period?

Short term or typical stack tests were conducted during the activated carbon injection phase. Two different activated carbon injection rates (120 and 300 mg/dscm) were evaluated during the test program. Several dose rates of Na2S4 were evaluated and two dose rates were selected (80 and 120 mg/Nm^3) for detail test evaluations. In addition, several test runs and a 36-hour continuous test were made while injecting 90 mg/Nm^3 of Na2S4 and 60 mg/dscm of activated carbon simultaneously.

Stack tests for Hg emissions were conducted using U.S. EPA Method 29. During parts of the testing program, a semi-continuous Hg analyzer which required daily reagent replacement and maintenance was used to assist in the evaluation program. BBP Environment developed the semi-continuous monitoring system to measure total Hg within the expected range of MWC operation. This system was used to measure the outlet Hg emissions during the Na2S4 only injection tests and during the tests performed while simultaneously injecting both Na2S4 and activated carbon.

Activated Carbon Only Injection

Activated carbon injection tests were conducted at feed rates of 120 and 300 mg/dscm. However, the combined tests with Na2S4 and activated carbon were run at 57.5-mg/dscm of activated carbon. We did not measure any emission data at the 57.5-mg/dscm activated carbon feed rate due to time limitations. The following is a summary of the activated carbon test:

Dose Rate Activated Carbon mg/dscm (No Na_2S_4)	Average Hg Inlet µg/dscm @ 7%O_2	Average Hg Outlet µg/dscm @ 7%O_2	Hg Removal
120	250	20	92.0%
300	210	5	97.6%

The activated carbon injection test results were compared with Licata Energy's activated carbon injection model and the pilot plant test results compared favorably with the model's projection. However, the actual test results showed slightly higher Hg removal than the model projects. Based on the test data and the use of our activated carbon modeling analysis, it was concluded that in order to meet a Hg emission limit of 28 µg/dscm without a percent reduction with a 95% confidence level, approximately 230 mg/dscm of activated carbon would be required.

Na2S4 Only Injection

We had two test series at 80 mg/Nm3 and three test series at 120 mg/Nm3. Each of the test series was conducted over several days using both the continuous monitor (outlet only) and manual stack test (inlet and outlet). The following is a summary of the Na2S4 only injection test:

Dose Rate Na_2S_4 - mg/Nm^3 (No activated carbon)	Average Hg Inlet µg/dscm @ 7%O_2	Average Hg Outlet µg/dscm @ 7%O_2	Hg Removal
80	148	26	82.4%
120	360	24	93.3%

Combined Test (Activated Carbon and Na2S4)

For the combined test, BBP Environment calculated that the optimum injection rate of 90 mg/Nm^3 would achieve the required Hg reduction.

Accordingly, a series of tests were conducted while simultaneously injecting Na2S4 at a dose rate of 90-mg/Nm^3 with activated carbon at a dose rate of 57.5 mg/dscm. During these tests, the inlet concentration of Hg ranged from 170 - 250 µg/dscm at 7% O2. All measured values at the outlet were below 20 µg/dscm at 7% O2. As part of this evaluation, the continuous Hg analyzer was used and the system was run for 36 hours in this condition.

Using our computer model, which predicts Hg removal efficiency by activated carbon, we determined that at a dose rate of 57.5 mg/dscm an 80.0% removal of Hg would be expected. Also, the estimated Hg removal efficiency at a Na2S4 only dose rate of 90 mg/Nm^3 was calculated to be 83.4% over the expected range of uncontrolled Hg emissions. The testing with simultaneous injection of activated carbon and Na2S4 showed Hg removal rates that ranged between 89.6% and 92.6%. Therefore, we conclude that the combination of activated carbon injection and Na2S4 was more efficient than either technology applied separately.

The combined application of Na2S4 and activated carbon showed that in order to achieve the 28 mg/dscm, the total activated carbon feed rate could be reduced from 230 to 57.5 mg/dscm resulting in a reduction in activated carbon usage of 18 lbs/hr. We have calculated that for an 800 TPD MWC (2 x 400 TPD lines), the annual cost of activated carbon would be $320,000. The Na2S4 solution would cost $176,000 per year resulting in an annual operating cost savings of $144,000. The total capital cost of the complete Na2S4 system would be between $285,000 and $325,000 with an annual cost of $28,500 to $32,500 per year. Even with the additional capital cost of the Na2S4 system, there is a substantial annual saving by using these two technologies in combination.

SUMMARY AND CONCLUSION

Both full scale and pilot plant tests have demonstrated that the Na2S4 system is both a technologically and an economically effective approach to controlling Hg emissions from waste combustion facilities. Pilot plant and short-term tests have verified that the Na2S4 technology alone or in combination with activated carbon technologies can achieve a controlled emission rate of 28 µg/dscm on MWCs equipped with a spray dryer and ESP. It would be beneficial to have a longer test program to optimize the dose rate of Na_2S_4 to control Hg emissions at these low levels. Since the efficiency of the Na_2S_4 is based on mass transfer, the technology would be even more effective on facilities equipped with fabric filters due to the additional retention and contact time.

When both the Peel and Avedøre complete their performance test this summer, our database will be increased. This expanded database will include new applications and significantly different concentrations of Hg emissions.

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