MERCURY CONTROL FOR MWCs USING THE SODIUM TETRASULFIDE PROCESS

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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 (Na_2S_4) 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 EPA's.

The original German Hg standard was $50~\mu g/Nm^3$ at 11% O_2 which is equal to $65~\mu g/$ dscm at $7\%~O_2$ EPA set the Hg emission limit for MWCs at $80~\mu g/$ 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/Nm³ at 11% O₂ using CEMS.

Several states have proposed or adopted a Hg emission standard of 28 $\mu g/dscm$ at 7% O_2 or 85% reduction which ever is less restrictive. The Commonwealth of Massachusetts has proposed a standard of 28 $\mu g/dscm$ 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 Na₂S₄ technology are:

- The reaction yields stable inert reaction products.
- Na₂S₄ is a liquid and is easier and safer to handle than powered activated carbon. Also, being a liquid, the feeding and control of Na₂S₄ 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 Na₂S₄ 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.

MERCURY FROM WASTE-TO-ENERGY PLANTS

At higher temperatures, mercury compounds are not very thermally stable, therefore, the mercury is gaseous at a temperature of 850°C 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:

$$HgO + 2 HCl \leftrightarrow HgCl_2 + H_2O$$
 (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 O₂, 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 Hg^o 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 1).

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 (Hg₂Cl₂):

$$2 \operatorname{Hg}^{0} + 2 \operatorname{HCl} + \frac{1}{2} \operatorname{O}_{2} \leftrightarrow \operatorname{Hg}_{2} \operatorname{Cl}_{2} + \operatorname{H}_{2} \operatorname{O} \quad (\operatorname{Eq}. 2)$$

• Elemental mercury can be oxidized to mercury oxide (HgO):

$$2Hg^0 + O_2 \leftrightarrow 2 HgO$$
 (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 HgO are not stable at temperatures above $400^{\circ}C$. Above this temperature, Hg_2Cl_2 decomposes into Hg^0 and $HgCl_2$ respectively and HgO into $Hg^0 + \frac{1}{2}O_2$.

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^oC, see Table 1). 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 Hg⁰ and 85 to 95% as HgCl₂. The elemental mercury portion can increase drastically in two ways:

1. as the amount of SO₂ exceeds the amount of HCl by an

- order of magnitude, or
- 2. if there is no residence time for the HgCl₂ 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 Hg⁰. A characteristic of both Hg⁰ and HgCl₂ is their high vapor pressure, even at temperatures as low as 200°C. 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

Beside 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.

Recently, alternative processes, especially for the separation of elemental mercury, have been proposed, 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 Na₂S₄ Process for Mercury Separation

The disadvantages of the various conventional processes as described above forced Steinmüller/BBP Environment to develop its own principle of mercury separation using Na₂S₄ which can capture both ionic HgCl₂ and Hg⁰ in accordance with the following simplified reactions:

$$Na_2S_4 + HgCl_2 \leftrightarrow HgS + 2NaCl + 3S^0$$
 (Eq. 4)

$$S^0 + Hg^0 \leftrightarrow HgS$$
 (Eq. 5)

It is sufficient to inject an aqueous Na₂S₄ solution into the flue gas duct and such a system can be easily retrofitted to an existing flue gas cleaning plant. The Na₂S₄ 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 1) and thus, effectively immobilizes the mercury by chemical binding. The black allotrope known as metacinnabarite is found in waste combustion facilities that, in the course of several years, changes into the stable red allotrope.

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 Na₂S₄ as aqueous alkaline liquids show a strong affinity towards the gaseous HCl.

The dissolved HCl will decompose the existing Na₂S₄ in the droplets as follows:

$$Na_2S_4 + 2 HCI \leftrightarrow H_2S + 3 S + 2 NaCl$$
 (Eq. 6)

After evaporation of the droplet, the H_2S injected into the flue gas is gaseous at a temperature of approximately $220^{\circ}C$. Elemental sulfur is then formed (melting point of sulfur = $119^{\circ}C$, boiling point = $445^{\circ}C$) (see Table 1) and exists in liquid form as an aerosol with a diameter of < 1 μ m.

However, it is most unlikely that the HCl will decompose all Na_2S_4 molecules. Because Na_2S_4 (melting point = $275^{\circ}C$) 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 H₂S^(g), S^{o (1)}, and Na₂S₄. According to the predominant opinion in literature and also according to the steam pressure curve for pure components, Hg^o and HgCl₂ 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 Hg⁰ and HgCl₂ are dissolved in the droplet of the additive where they react as follows:

$$HgCl_2 + H_2S \leftrightarrow HgS + 2 HCl$$
 (Eq. 7)

$$Hg^0 + S^0 \leftrightarrow HgS$$
 (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 Hg⁰ and HgCl₂: - 40^oC and 280^oC, boiling temperature: 360^oC and 303^oC) (see Table I) to account for the presence of Hg⁰ and

HgCl₂ 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:

$$HgCl_2 + Na_2S_4 \leftrightarrow HgS + 2 NaCl + 3 S^0$$
 (Eq. 9)

$$Hg^0 + Na_2S_4 \leftrightarrow HgS + Na_2S_3$$
 (Eq. 10)

According to Eq. 7, $H_2S^{(g)}$ can react to form HgS in the gaseous phase as well as in the liquid phase with the HgCl₂ aerosols. $S^{0,(1)}$ 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 fed sulfur 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^o and HgCl² during the entrained-flow phase that is started by the reaction of Na₂S₄ with the dissolved HCl (see Table 2).

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 3). The most recent project is described in the following section.

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 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 limits, 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 SO₂, and imposed new emission limitations for mercury, cadmium, lead and NOx. The present APC system meets all the new emission

limitations with the exception of the ones for PCDD/PCDF, mercury and NOx 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 NOx emissions to the newly required levels if the facility was to be expanded.

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

The details of the project were presented in the paper titled "Retrofit of a WTE with SCR for NOx and PCDD/F Control and Na₂S₄ 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 NOx and dioxins and to install a Na₂S₄ system for Hg control in order to meet a mercury emission limit of 50 μ g/Rm³ at 11% O2 (65 μ g/dscm at 7% O₂) with no percent reduction provision.

The Na₂S₄ system consists of a mixing and dosing station and a lance to inject the Na₂S₄ solution into the ductwork. The Na₂S₄ is purchased in a 34% to 40% concentrated solution in 55 gallon barrels or 1 m³ containers. In the mixing station, the Na₂S₄ 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 in the vicinity of 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 m³/h (STP, wet) 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 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.

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.

The Na₂S₄ process was selected due to the high mercury inlet concentration of 1.1 mg/Nm³ @ 11% O₂ (design value) which has to be controlled to below 50 μ g/ Nm³ @ 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 (Hg⁰) and ionic mercury (Hg²⁺) 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/Nm³) for detail test evaluations. In addition, several test runs and a 36-hour continuous test were made while injecting 90 mg/Nm³ 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 ₂ S 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 $28~\mu g/dscm$ 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 ₂ S 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/Nm³ would achieve the required Hg reduction.

Accordingly, a series of tests were conducted while simultaneously injecting Na_2S_4 at a dose rate of 90-mg/Nm³ with activated carbon at a dose rate of 57.5 mg/dscm. During these tests, the inlet concentration of Hg ranged from 170 - 250 μ g/dscm at 7% O_2 . All measured values at the outlet were below 20 μ g/dscm at 7% O_2 . 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/Nm³ 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 Na_2S_4 and activated carbon showed that in order to achieve the 28 µg/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 Na_2S_4 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 Na_2S_4 technology alone or in combination with activated carbon technologies can achieve a controlled emission rate of 28 μ g/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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TABLE 1 Selected Physical Properties of Hg and Hg Compounds

				'Meta-Cinnabarite'			
				(black, meta-stable)			Sodium
	Mercury	Calomel	Sublimate	'Cinnabar' (red, stable)	Mercury-oxide	Sulfur	tetrasulfide
	(\mathbf{Hg}^0)	(Hg_2Cl_2)	$(HgCl_2)$	(HgS)	(HgO)	(S)	(Na_2S_4)
Melting temperature	38 84	Solid	080	7:100	Colid	118 05	275
(°C) at $p = 1$ atm.	-20.04	SOIIG	707	20110	DOLLO	6.011	213
Boiling temperature	36 958		303			9 777	
(°C) at $p = 1$ atm.	00.000		COC			0.1	
Sublimation							
temperature (°C) at		383		580			
p = 1 atm.							
Vapor pressure	0.0017 mbar						
at p = 1 atm., 20°C	_13,000 μg/m³					-	
Formation/				Decomposition, oxidizing	Formation 300-350 °C		
Decomposition		To the second		atmosphere & $\geq 400^{\circ}$ C	Do.		

TABLE 2 Results Of Trial Run With Na₂S₄ Injection Kassel Waste-to-Energy Plant, November 1995

													_
	100	canc.		Hg ²⁺	74	46	50	77	64	43	63	17	55
	Domoval Reficiones	(%)		Hg ⁰	92	98	95	86	82	82	85	96	89
	Domo			Hgges	79.5	63	65	83	- 69	47.5	99	56	99
		oution	(9)	Hg ²⁺	88	85	95	- 64	91	96	94	96	93
	50	Distribution	(%)	Hg ⁰	12	15	5	3	6	4	9	4	7
r GmbH	Clean Gas	, ,		Hg^{2+}	14	23	19	35	42	51	44	24	32
teinmülle		Content	(µg/Nm³)	Hg^0	2	4	1	1	4	2	3	1	2
L. & C. Steinmüller GmbH	-			Hgges	16	27	20	36	46	53	47	25	34
_		bution	(%)	Hg ²⁺	19	62	<i>L</i> 9	73	84	68	98	51	72.5
		Distril	<u>6</u>)	Hg ⁰	31	38	33	27	16	11	14	49	27.5
	Raw Gas			Hg^{2+}	54	45	38	154	116	06	118	29	81
		Content	(μ/m^3N)	Hg ⁰	24	28	19	58	22	11	20	28	29
				Hgges	78	73	57	212	138	101	138	57	107
				No.	-	2	3	4	5	9	7	∞	Mean

TABLE 3 Flue Gas Cleaning Systems With Na₂S₄

Plant	Kassel MHKW	Gevudo	VERA Hamburg	RVA Boehlen
		Dordrecht INL)	
Fuel	MSW & commercial waste	MSW	Sewage sludge	Hazardous waste
Capacity/	2 x 10 t/hr	4 x 7.5 t/hr	2 x 3 t/hr. (dry solids)	1 x 3.33 t/hr
Flue gas flow rate	$2 \times 65,000 \text{ m}^3/\text{hr (wet)}$	$2 \times 130,000 \text{ m}^3\text{/hr (wet)}$	$2 \times 21,200 \text{ m}^3/\text{hr (wet)/3 lines}$	$1 \times 30,000 \text{ m}^3/\text{hr (wet)}$
Na ₂ S ₄ Purpose	• Hg sink	Minimization of coke addition upstream of entrained flow FF	Hg sink Preliminary Hg capture	
	rg iiiiii00iiiization	Hg immobilization	quality gypsum	
Hg in uncontrolled flue gas (mg/Nm³)	0.2 – 0.6	0.7	1.35	0.9
Start-up	March 1997	Nov. 1996	Dec. 1996	Sept. 1997

FIGURE 1 PROCESS DIAGRAM, PEEL PROJECT

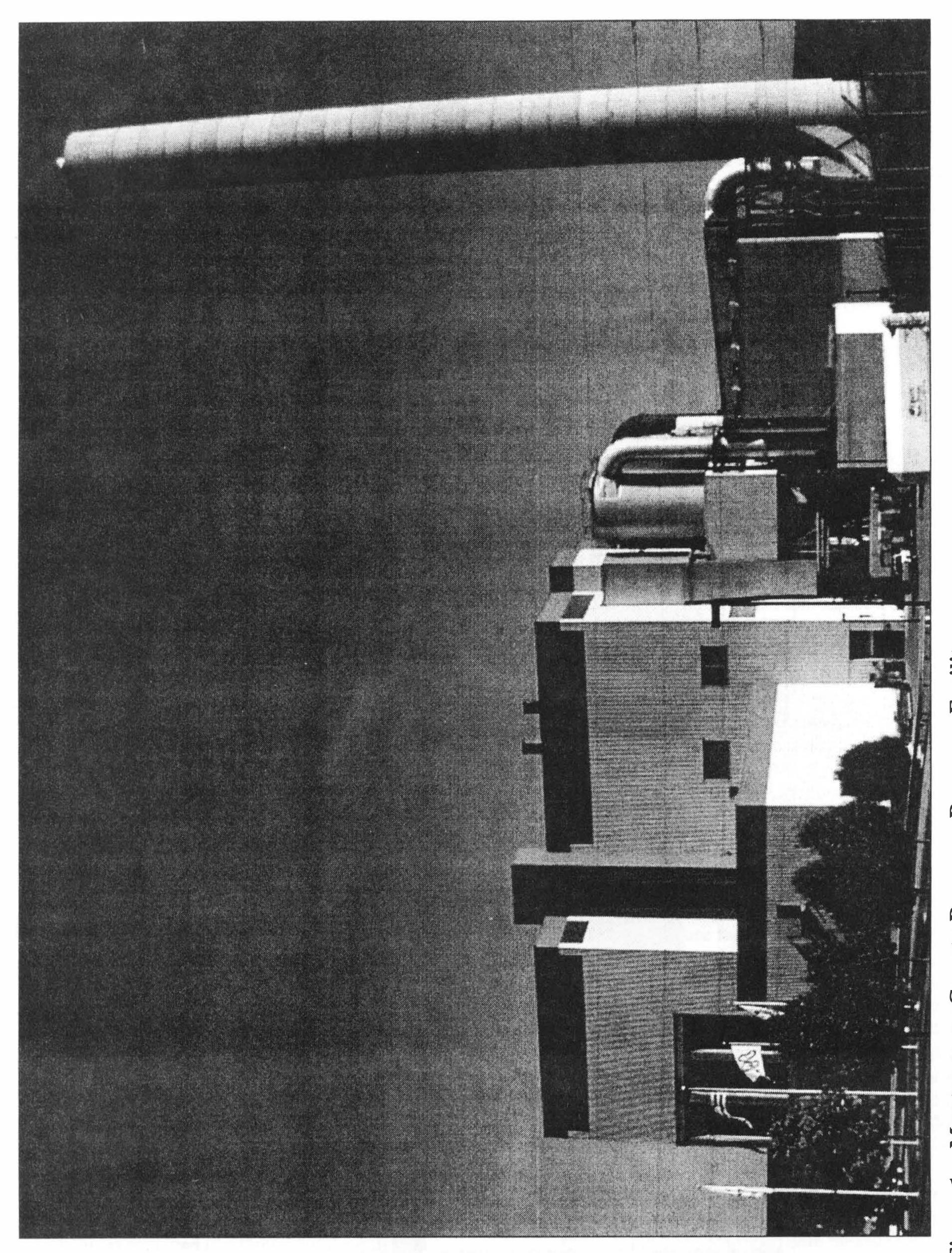


Figure 1 - Montgomery County Resource Recovery Facility

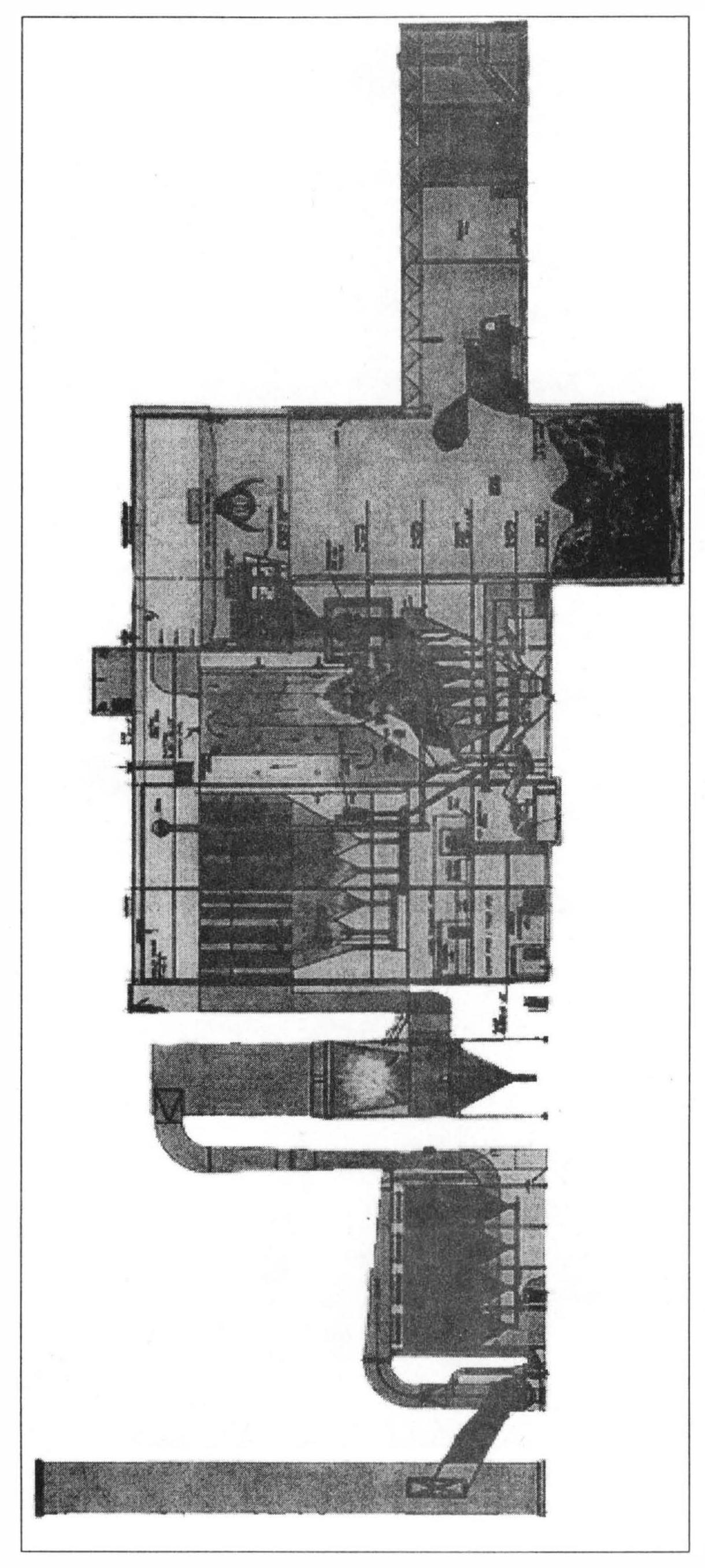


Figure 2 - Facility Cross Section