1 of 1

ANL/ES/CP--81850
Conf-940952--1

ARGONNE NATIONAL LABORATORY
9700 SOUTH CASS AVENUE
ARGONNE, ILLINOIS 60439

ELEMENTAL MERCURY REMOVALS OBSERVED IN A LABORATORY-SCALE WET FGD SCRUBBER SYSTEM

by

M.H. Mendelsohn, J. Wu, H. Huang, and C.D. Livengood
Energy Systems Division
Argonne National Laboratory
Argonne, Illinois 60439, U.S.A.

DISCLAIMER

Emerging Clean Air Technologies and Business Opportunities
September 26-30, 1994
Toronto, Canada

ELEMENTAL MERCURY REMOVALS OBSERVED IN A LABORATORY-SCALE WET FGD SCRUBBER SYSTEM

M.H. Mendelsohn, J. Wu, H. Huang, and C.D. Livengood
Energy Systems Division
Argonne National Laboratory
Argonne, IL 60439, U.S.A.

ABSTRACT

Published data are limited regarding gaseous mercury removal in wet scrubber flue-gas desulfurization (FGD) systems. The data that do exist show a wide variation in reported mercury removals, from about 5 to 95%. We have performed tests for the removal of gaseous elemental mercury in a well-controlled laboratory environment by using both conventional and modified configurations of an aqueous scrubber system. Results from these tests strongly suggest that the removal of elemental mercury in a wet scrubber system is controlled by liquid-film resistance. Our results have also led us to hypothesize that the mercury-containing species in a flue-gas stream consist of only two types: elemental mercury and oxidized mercury compounds. We further assert that the differences observed in mercury removal reflect different proportions of each of these two types of mercury-containing species. We suggest that the total mercury removal will be high when the actual, but unmeasured, proportion of oxidized mercury compounds is high.

INTRODUCTION

Although coal-fired electric utility boilers have not been considered to emit significant amounts of gaseous mercury, the measurement and control of this element and its compounds is of considerable interest.[1] In fact, mercury has been singled out for a separate Environmental Protection Agency study that will examine emissions from utility and other sources, health and environmental risks, and control technologies, including their cost.

Although a lot of information is not available in the literature regarding the removal of gaseous mercury from coal-fired boilers, the available data do show a wide variation in reported gaseous mercury removal with wet flue-gas-desulfurization (FGD) scrubber systems. A recent review of published data on mercury emissions from coal-fired boilers [2] reported mercury removal efficiencies ranging from 10 to 95% with wet FGD systems. Also, according to a recent report on coal-fired power plants in

The Netherlands, researchers found gaseous mercury removals ranging from 8 to 72% across several different wet FGD systems.[3] Because differences in system design or operating parameters may not explain such widely varying results, the question naturally arises as to the cause of this wide disparity across various wet FGD systems.

Aside from possible errors in accuracy or reliability, a serious shortcoming in the earlier reported data is that, in general, no speciation has been done on the mercury present in the flue gas. That the mercury in flue gas may exist as many different chemical species is an important consideration. For example, mercury may exist as relatively volatile elemental mercury or, perhaps, as somewhat less volatile oxidized species, such as mercuric or mercurous chloride. Recent studies have recognized the importance of analytically determining the concentration of individual mercury species [4,5], but, to date, the possible differences in removal behavior of different gaseous mercury species in a wet scrubber system have not been systematically studied.

In our laboratory, we have been studying the removal of low levels of gaseous elemental mercury by means of solid adsorbents, such as activated carbon [6], and wet scrubber removal of sulfur dioxide and nitrogen oxides [7]. Therefore, we decided to try and measure the removal of a low level of gaseous elemental mercury by using an aqueous scrubber system in a well-controlled laboratory experiment. Using several different scrubber solutions, we observed that no elemental mercury was removed in a laboratory-scale wet scrubber system under conditions similar to those that yielded about 90% removal of sulfur dioxide when a hydrated lime scrubber solution was used. This testing used what we describe as a "conventional" wet scrubber configuration.

After these initial tests, further testing was performed by using two "nonconventional" scrubber configurations: (1) adding two different types of packing material to the scrubber column and (2) using two different types of gas-diffusion devices for injecting test gas into the scrubber solution. These changes to the original scrubber system have greatly increased the amount of elemental mercury removed from 5 to 40%. Very recently, we have obtained mercury removals of 40-80% by using a solution containing a substance that is apparently very reactive with elemental mercury. These latter results await confirmation by further testing.

The results summarized above provide us with an insight into the mechanism that might be responsible for determining the amount of elemental mercury removed in an aqueous scrubber system. These results also lead us to suggest a hypothesis for the widely

varying mercury removals observed by previous workers. To summarize this hypothesis, we suggest that varying the proportions of elemental and oxidized mercury components in different flue-gas streams affects mercury removal. Because the percentage of removal may be high for certain highly soluble oxidized mercury compounds, such as mercuric chloride, and conventional wet scrubber conditions have not removed elemental mercury, reported high mercury removals may have been possible with flue-gas streams containing a high proportion of mercuric chloride. Conversely, flue-gas streams containing a high proportion of elemental mercury may yield low mercury removals.

EXPERIMENTAL DESIGN and RESULTS

In this note, the more salient features of the experimental system are described. A more detailed description of the two separate systems that were combined for these tests has been given elsewhere.[6,7] The two previous systems used (that is, the low-level mercury preparation/fixed-bed absorber and aqueous scrubber systems) were combined by connecting the outlet side of the mercury-preparation system to the gas inlet line of the aqueous scrubber system by using 1/4-in.(0.635-cm) diameter Norprene tubing. The analytical instrument was a Jerome 431-X gold-film mercury-vapor analyzer, with a resolution of 1 $\mu g\ Hg/m^3$ and a sensitivity of 3 $\mu g\ Hg/m^3$. The specified accuracy is ±5% at 100 $\mu g\ Hg/m^3$. This instrument was placed downstream of the exit from the wet scrubber column and was protected by one or two ice-water traps.

The diameter of the wet scrubber column was 7.6 cm, and its height, measured from a sieve plate (with 0.476-cm-diameter holes) at the bottom of the column to the bottom of the liquid inlet nozzle at the top of the column, was 52.7 cm. Baseline mercury concentrations were first measured in all tests without any liquid flowing through the scrubber column. Preliminary tests were performed by using a conventionally configured scrubber system.[7] (To distinguish the conventional configuration from later tests, no packing and no special gas-diffusion device, other than the sieve plate described above, were used.) Three different types of scrubber solutions were tried in the preliminary tests: ordinary distilled water, saturated calcium hydroxide solutions, and a potassium polysulfide solution. Several different process conditions were tested, including varying the liquid column height in the scrubber from 12 to 43 cm, with a scrubber liquor temperature of either 22 or 50°C. Baseline mercury concentrations ranged from 39 to 42 $\mu g\ Hg/m^3$. Under the conditions described above, no measurable mercury vapor was removed. We estimate that

a removal of at least 5% would be required to be outside of the specified accuracy of the instrument. However, in no case was a measurement recorded that was even 1 μg Hg/m^3 lower than the baseline concentration.

After the preliminary tests, the configuration of the scrubber column was changed to test two different packing materials and two different gas-diffusion devices. In these tests, distilled water was used, and the pH was adjusted, as necessary, with sodium hydroxide. Also, the baseline mercury concentration in the test gas ranged from 90 to 120 μg Hg/m^3. We estimate that a removal of at least 3% would be required to be confident that the measured difference exceeds the analytical instrument's sensitivity. Several tests were performed with 3/8-in. (0.953-cm) ceramic saddle packing from the Norton Company and 0.24-in. (0.610-cm) stainless-steel packing from the Scientific Development Company. Mercury removal with the ceramic packing increased to 4-6% at a pH ranging from 5 to 12. However, this packing material could not be tested with a polysulfide solution, because small amounts of hydrogen sulfide were produced, and the analytical instrument was sensitive to this interfering gas.

Stainless-steel packing was then used to avoid the problems associated with the ceramic packing. Interestingly, significant removal (11% with about 15 cm of packing and 21% with about 28 cm of packing) was achieved with only the dry packing in the column. Removal with a wet packing (distilled water with a pH ranging from 5 to 12) ranged from 15 to 20%. Adding polysulfide anions to the scrubber solution appeared to increase the wet packing removal to about 40% (when both 15 cm and 28 cm of packing was used, removal was approximately the same).

Next, a coarse, spherical, 2.5-cm-diameter gas-diffusion stone was used to introduce the test gas to the scrubber column. The average pore size of a coarse-glass frit is nominally 60 μm. Tests were performed with and without packing and with and without polysulfide anions in the scrubber solution. In all four cases, mercury removal was 24% ± 2%. Also, several tests were performed with a 4-cm-diameter medium-porosity gas-diffusion disc (a flat plate). In this case, the pore size is specified as 10-15 μm. With this gas-diffusion device, the mercury removal was about 16%.

Finally, we have recently discovered an additive to an aqueous scrubber solution that improves the percent of mercury removed (with the 4-cm gas-diffusion disc described above) to about 40-80%. This result has not been confirmed and will be reported after further study.

DISCUSSION

It is well known that the rate-controlling step in wet scrubber systems having a gas-liquid interface may fall into one of two limiting cases. For a sufficiently soluble gaseous species, the removal may be gas-film limited, while for a less-soluble species, the removal rate may be controlled by the liquid-film resistance. For example, it is known that the removals of SO_2 and NO are gas-film and liquid-film controlled, respectively.[8] By using a saturated calcium hydroxide scrubber solution, we have achieved SO_2 and NO removals of about 90% and 1-2%, respectively, We were, however, able to increase the removal rate of NO to 60-70% by adding ferrous ethylenediaminetetraacetic acid to the scrubber solution, which reacts rapidly with dissolved NO and thus reduces the liquid-film resistance.[7] Similarly, because elemental mercury is even less soluble than NO (0.018 versus 4.0 mg/100 mL at 50°C), we expected only minimal mercury removal in either ordinary distilled water or a saturated calcium hydroxide solution.

Indeed, our preliminary results indicated that using conventional aqueous scrubber conditions (described above) will not yield detectable elemental mercury removal. However, as might be expected for a situation that is liquid-film controlled, adding packing or decreasing bubble size (by using a gas-diffusion device) did significantly improve mercury removal. Because of varying pressure and flow conditions in our tests, we are unable to quantify the results we have obtained thus far. However, the trends are clear and indicate that without significantly changing the liquid-film resistance, elemental mercury removal in an aqueous scrubber system will be minimal.

Polysulfide solutions have been reported capable of greatly increasing the percentage of gaseous mercury removed.[9] Our preliminary tests, with the addition of polysulfide anions to the scrubber solution, did not show any improvement. Also, no improvement was noted in the tests with a gas-diffusion device. Therefore, we feel that the conclusion that polysulfide anions can enhance an aqueous scrubber system's performance in terms of mercury removal must be viewed with caution. However, we did observe a significant improvement in mercury removal with stainless-steel packing and polysulfide solutions (Note: stainless-steel packing was also used in the tests referred to above[9]). Therefore, it may be that a synergism exists between the stainless-steel packing and polysulfide anions that does not exist under other conditions with polysulfide anions. Understanding the mechanism or mechanisms involved in mercury removal with stainless-steel packing and a scrubbing solution are

complicated by the fact that a significant mercury removal was noted for the dry packing alone (11-20%, as noted above). The possibility of using other additives that may react with dissolved mercury even more rapidly than polysulfide also needs to be considered. Indeed, preliminary results indicate that we may have discovered a substance capable of significantly improving mercury removal performance in an aqueous scrubber system. Further details on this additive will be presented at a later time.

As a result of our research, we have formulated a hypothesis for the widely varying mercury removals reported in the literature for commercial wet FGD systems. We assume that the mercury species in a flue-gas stream may be broadly classified into two types of compounds with different aqueous-solubility properties. We will assume that a mercury-containing flue gas will consist only of either elemental mercury or oxidized mercury, typified by mercuric chloride. Because of the high solubility of mercuric chloride, we assume that it, along with the gaseous SO_2, can easily be removed in a wet scrubber system. Experimentally, we have shown that removing elemental mercury is very difficult in a conventional wet scrubber system. Therefore, we can explain the widely varying reported removals in a wet FGD scrubber system by asserting that the removal of total mercury will be proportional to the amount of oxidized mercury in the incoming gas stream. In equation form, we assert the following:

$$R \propto \{HgCl_2\}/[\{HgCl_2\} + \{Hg^\circ\}], \text{ where}$$

R = total gaseous mercury removed (where R ranges from 0 to 1), $\{HgCl_2\}$ = total concentration of gaseous oxidized mercury compounds, and $\{Hg^\circ\}$ = total concentration of gaseous elemental mercury.

Mercury removal data have recently been published by Noblett et al.[4] Their data show 86-97% total mercury removal across a pilot-scale wet scrubber system. More importantly, they have analyzed their mercury as separate oxidized and elemental mercury concentrations both at the inlet and at the outlet of the wet scrubber. From the data in their Table 4, we have calculated the percent of total mercury removed that is due to the removal of oxidized mercury. As can be seen in Table 1 (which is based on Noblett et al.'s Table 4), on average, 99.7% of the total mercury removed can be attributed to the removal of oxidized mercury. Not only is this in agreement with our hypothesis described above, but it is also consistent with the approximately zero rate of removal for gaseous elemental mercury we observed in our conventionally configured laboratory scrubber system.

Table 1: GASEOUS MERCURY REMOVAL VALUES GENERATED FROM DATA IN REF. [4]

Total mercury removed ($\mu g/Nm^3$)	Total oxidized mercury removed ($\mu g/Nm^3$)	Percent of total mercury removed due to oxidized mercury (%)
8.43	8.27	98.1
8.41	8.32	98.9
10.29	10.36	100.7
6.79	6.89	101.5
7.59	7.53	99.2
9.19	9.22	100.3
7.60	7.55	99.3
		Average = 99.7

CONCLUSIONS

We have found that low levels of gaseous elemental mercury are difficult to remove in a conventionally configured laboratory-scale aqueous scrubber system. Higher levels of elemental mercury can be removed by modifying the wet scrubber configuration to reduce liquid-film resistance (e.g., by adding packing material to the scrubber column or by increasing the gas-liquid contact area by reducing bubble size). The observation of very low elemental mercury removal in a conventional aqueous scrubber system, along with a presumed variation in the concentration of the mercury species in different flue-gas streams, can explain the wide differences observed to date in the mercury removal performance reported in the literature for wet FGD scrubber systems.

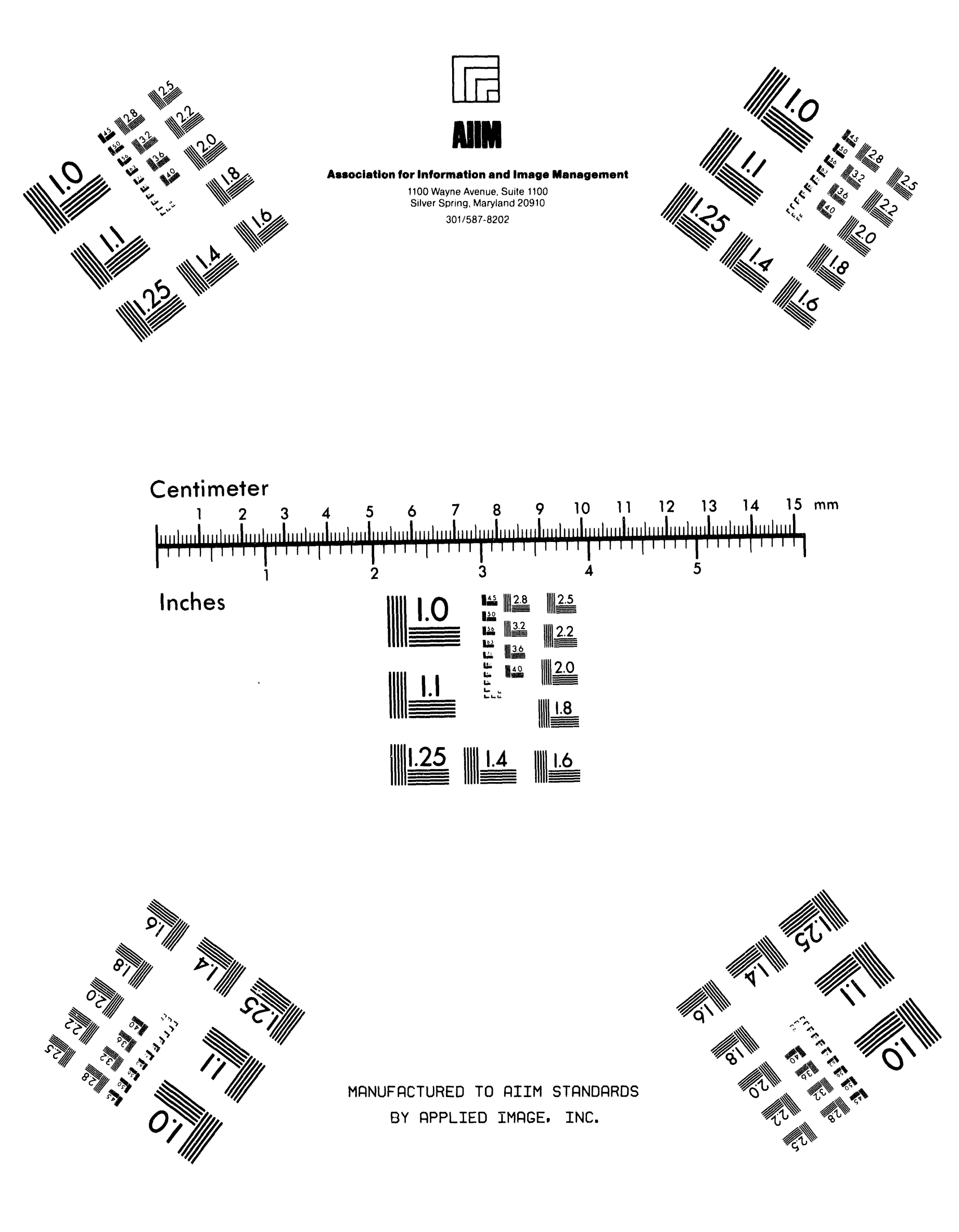
ACKNOWLEDGMENTS

This work is supported by the U.S. Department of Energy, Assistant Secretary for Fossil Energy, under contract W-31-109-ENG-38, through the Pittsburgh Energy Technology Center (PETC). We acknowledge the support provided by Perry Bergman and Charles Drummond of the PETC. In addition, we wish to express our thanks to Sherman Smith for his assistance in performing some of the tests described above.

REFERENCES

1. D. Boutacoff, "New Focus on Air Toxics," EPRI Journal, March 1991.

2. H.S. Huang, C.D. Livengood, and S. Zaromb, "Emissions of Airborne Toxics from Coal-Fired Boilers: Mercury," Argonne National Laboratory, Argonne, IL, Sept. 1991.
3. R. Meij, *Water, Air, and Soil Pollut.*, 56:21-33, 1991.
4. J.G. Noblett, Jr., F.B. Meserole, D.M. Seeger, and D.R. Owens, "Control of Air Toxics from Coal-Fired Power Plants Using FGD Technology," Second International Conference on Managing Hazardous Air Pollutants, Washington, D.C., July 13-15, 1993.
5. K. Felsvang, R. Gleiser, G. Juip, and K.K. Nielsen, "Air Toxics Control by Spray Dryer Absorption Systems," Second International Conference on Managing Hazardous Air Pollutants, Washington, D.C., July 13-15, 1993.
6. C.D. Livengood, H.S. Huang, and J.M. Wu, "Experimental Evaluation of Sorbents for the Capture of Mercury in Flue Gases," 87th Annual Meeting of the Air & Waste Management Association, Cincinnati, OH, June 19-24, 1994.
7. M.H. Mendelsohn and J.B.L. Harkness, *Energy & Fuels*, 5:244-8, 1991.
8. P. Harriott, K. Smith, and L.B. Benson, *Environ. Progr.*, 12:110-13, 1993.
9. T.Y. Yan, *Ind. Eng. Chem. Res.*, 30:2592-5, 1991.


AIIM
Association for Information and Image Management
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202
Centimeter
Inches
MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

DATE
FILMED
12/19/94

END