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Mercury-Binding Materials
for Flue Gas Cleanup   TPL-FR-2151/ER36(Ph I)
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MERCURY-BINDING MEMBRANES
FOR FLUE GAS CLEAN-UP

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Final Report
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1. EXECUTIVE SUMMARY

All Phase I objectives were met. In the Phase I program, TPL developed a material, T-450, capable of removing elemental mercury from air. It was found to have high porosity, good mechanical strength, good affinity for aqueous ionic mercury, and good stability to hot acidic gas. The material, used as a granular solid, was tested for adsorption of mercury in two protocols, one involving static room-temperature air and one using flowing hot air. In each case, it was superior to activated carbon.

The following results were obtained:
1. Sol-gel methods were found to be applicable for synthesis of silicates containing oxidized thiol (disulfide) groups.
2. Synthetic parameters were determined for silicates with a variety of physical properties and performances.
3. Measurement of physical properties indicate high porosity strength, and stability to conditions found in flue gases.
4. The Hg° adsorption of T-450 was superior to that of activated carbon; static testing indicated a 2.4-fold increase in mercury adsorption, while a flow system mimicking hot flue gas indicated a 3.6-fold increase in Hg adsorption.
5. Economic analysis indicated that T-450 is a strong candidate for scale-up and commercial development. For the cost of removing Hg from flue gas, a savings of 23.5% is estimated, relative to use of activated carbon.

2. INTRODUCTION AND BACKGROUND

The U.S. Environmental Protection Agency (EPA), in its December 1997 Mercury Study Report to Congress,[i] estimated that 158 tons of mercury (Hg) are released annually into the atmosphere by anthropogenic sources in the United States; 87% of this is from combustion point sources. Four specific categories: coal-fired electric power plants (33%), municipal waste incinerators (18%), commercial and industrial boilers (18%), and medical waste incinerators (10%) account for about 80% of total Hg release. Power plant flue gases contain from 1 - 25 μg Hg per dry standard cubic foot (dscf), while medical waste incinerators contain 400 - 1400 μg Hg/dscf. The mercury is eventually precipitated or washed out of the air by rainfall, and returns to pollute soil and surface water. Mercury and its compounds are potent neurotoxins, with acute exposure to high levels, as well as chronic exposure to lower levels, causing severe physical symptoms, birth defects, and death. Nationwide, many streams and lakes have been polluted by mercury, to the extent that it is no longer safe to eat fish caught in them, since eating fish is the principal means of ingesting mercury.

The EPA has established Hg emission standards for municipal waste combustors (MWCs) and medical waste incinerators (MWIs). For coal-fired power plants, EPA will propose pollution control technologies and possibly a mercury trading scheme by 2003, and a final regulation by 2004; they will require pollution controls by November 2007, or earlier.[ii] Power plant operators may then be faced with requirements to greatly reduce the mercury concentration of their flue gases. The EPA has estimated a $5 billion cost, using available technology, for a 90% reduction of Hg emissions from the nation's 1043 utility boilers at 426 facilities; this is from $67,700 to $70,000 per lb of Hg removed (ref. 1, vol. VIII, p. ES-14).

Incinerators are also searching for more cost-effective means of reducing Hg emissions. Existing technologies are better suited for the 129 U.S. MWCs and 2400 MWIs; costs range from $211 to $870 per pound of Hg removed for MWCs, and $2000 to $4000 for MWIs. The potential national annual cost of mercury removal is over $100 million for these two industries. There is a need for a cost-effective technology to remove mercury from flue gases of MWCs and MWIs as well as coal-fired power generators.

3. PHASE I OBJECTIVES

In its Phase I proposal, TPL proposed to synthesize and evaluate a series of silicate materials covalently modified to contain organic groups capable of binding mercury, both elemental and ionic. Silica, the main compound found in common sand, has the chemical formula SiO_2, and consists of a solid matrix of silicon atoms, each surrounded by four oxygen atoms. The silicon atoms are linked by Si-O-Si bonds. Silica can be synthesized by condensation of silicic acid, $Si(OH)_4$, which is readily generated by hydrolysis of tetraalkoxysilanes. Thus, two Si-O-H groups become one Si-O-Si and one H-O-H, with the process continuing until all Si-O-H groups have reacted. It has been shown that similar condensation can occur with the Si-O-H groups of molecules containing three hydroxyl groups and one alkyl group. The precursor molecule 3-mercaptopropyl trimethoxysilane (henceforth abbreviated TMSi-SH) was selected as a candidate, because it is capable of condensation into a solid silicate, and it has an organic group capable of binding mercury atoms.

However, mercapto groups R-S-H are best suited for mercury ions, rather than elemental mercury atoms. Ideally, a material could both oxidize elemental mercury and bind it. Disulfides R-S-S-R experience two-electron reduction to two thiolate ions R-S⁻, while mercury ions experience two-electron oxidation to Hg^{2+}. Then, the two thiolate ions can bond to the mercury ion to form a R-S-Hg-S-R linkage. The goal of the program, then, is to produce silicates with disulfide groups generated from TMSi-SH. Condensation of four such TMSi-SH molecules gives the following product, shown after binding one mercury atom:

The above structure can be regarded as a before-and-after view, with the disulfide group on the left two silicons illustrating a disulfide group before reaction with mercury, and the group on the right two silicons showing the results of oxidizing and subsequently binding one mercury atom. This material, when polymerized into a large porous network, is a solid, capable of removing mercury contamination from a gas stream. In the structure shown above, all silicon atoms have 3-mercaptopropyl groups. Previous TPL work has indicated that such organic-rich materials have poor physical properties such as porosity and strength, and dilution with inorganic groups based on SiO_2 greatly improve these properties, at the cost of reduced concentration of active organic groups. So, in a more realistic sketch, only about one-fourth of the silicon atoms would have organic groups, with the remainder having only hydroxyl groups.

Accordingly, Phase I efforts were directed toward synthesis and evaluation of materials with this structure. Silicates having 3-mercaptopropyl groups covalently attached to the silica framework were labeled T-350, while those having disulfide groups from *oxidized* 3-mercaptopropyl groups were termed T-450.

3.1 PHASE I TECHNICAL OBJECTIVES

The goal of Phase I work was to conduct tests to demonstrate the effectiveness of T-350 and T-450 for removing Hg from flue gases resulting from both coal-fired power plants and waste incinerators, to demonstrate its efficiency and applicability to solving problems of interest to the DoE and private industry. A prerequisite to this goal was production of sufficient quantities of the most promising formulations of T-350 and T-450 for such evaluations. TPL's T-350 and T-450 are components of complete treatment systems. Phase II work will focus on more specific applications.

Phase II technical objectives were:
1.	Synthesize several formulations of T-350 and T-450 with promising properties;
2.	Test these formulations for chemical and physical properties;
3.	Determine which industrial applications are most applicable to TPL products; and
4.	Test formulations with optimal properties in a simulated flue gas system;

3.2	TECHNICAL APPROACH

TPL performed four sets of experiments to achieve the objectives listed above: to synthesize several formulations of T-350 and T-450 with promising properties (Objective 1), to test these formulations for chemical and physical properties (Objective 2), to determine which industrial applications are most applicable to TPL products (Objective 3), and to test formulations with optimal properties in a simulated flue gas system (Objective 4).

4. PHASE I EXPERIMENTAL PROCEDURES AND RESULTS

4.1 TASK 1: GENERAL SYNTHETIC PROCEDURES FOR THIOL-BASED SOL-GELS

Early experiments showed that the following general procedure was suitable for producing the desired sol-gel silicates with mercury-binding groups covalently attached.

1.   First, a solution of thiol-containing alkoxysilane is oxidized to a disulfide containing the corresponding alkoxysilane. Variables to evaluate included nature of oxidizer, ratio of oxidizer to thiol, and method of adding oxidizer.

2.   This disulfide-containing alkoxysilane, combined with one or more "inert" (*i.e.*, lacking mercury-binding functional groups) silicate precursors such as tetraethoxy orthosilicate or methyl trimethoxysilane, is then hydrolyzed under acidic catalysis. Variables to evaluate included amount of acid catalyst, amount of water, ratio of thiol to total silicon, nature and amount of other "inert" functional groups, and time and temperature of hydrolysis.

3.   The pH of the hydrolysate is next raised, thereby forming a gel.

4.   Final processing involves washing, drying, and sizing the solid material. This may involve washing with either ethanol or water, and fabrication to the desired shape and size.

Each of these steps is described in more detail in subsequent sections (4.1.1 through 4.1.4, respectively).

It is apparent that there are many parameters that must be properly set to achieve optimal performance. To determine which reaction conditions are most sensitive, and how they affect properties of the products, a series of Plackett-Burman screening experiment was performed. Plackett-Burman runs enable evaluation of the *general* effect of a number of binary parameters, in a fairly low number of reactions. Examples of binary parameters include stirring or not stirring, adding 50% more of a reagent or not adding more, and neutralizing with ammonia or potassium hydroxide. Typically, up to seven parameters can be evaluated in an eight-reaction design, or up to eleven parameters in a twelve-reaction design. Algebraic analysis of the results indicates which parameters are most significant, and the effects resulting. After Plackett-Burman results indicate general effects of altering parameters, the optimal values of the parameters are determined by more specific experiments.

After a series of Plackett-Burman reactions was performed, the products were dried, ground up, and sieved. Quarter-gram samples of material either passing a 10-mesh sieve but retained on an 18-mesh sieve, or passing an 18-mesh but retained on a 45-mesh sieve, were tested together for elemental mercury capacity by being sealed in a desiccator with an open bottle of mercury, for at least two days. Then, each silicate sample was placed in a 16 x 125 mm glass test tube, along with 2 mL of cold double-distilled concentrated aqueous nitric acid. After

the initial violent reaction had subsided, the tubes were heated at 70 °C for three hours, and cooled. Acid extracts were removed, and the silicates were washed repeatedly with deionized water. Acid extracts and washings were combined in 100-mL volumetric flasks, and brought to volume. Triplicates of 100-µL aliquots were analyzed for mercury by cold-vapor atomic absorption spectrometry.

4.1.1 Iodine Oxidation of Thiol Groups

In principle, mercaptopropyl groups can be oxidized either before or after sol-gel polymerization. However, oxidation of the thiol groups after polymerization was avoided, because it was feared that some thiol groups in the solid matrix would be unable to find another thiol group in its locality. Reaction of thiols in the form of a solution of 3-mercaptopropyl trimethoxysilane (TMSi-SH) was selected, to overcome this proximity problem. Furthermore, sol-gel polymerization of the oxidized disulfide would ensure that the solid matrix would position all sulfur atoms close enough for facile reaction with a gas-phase mercury atom.

Iodine was selected for the oxidation, because stronger oxidizers run the risk of over-oxidation to a sulfonate. The reaction of two thiols with iodine yields one disulfide compound and two molecules of hydrogen iodide. This production of an acid is somewhat desirable, because the subsequent hydrolysis of the silicon alcoxide is acid-catalyzed. However, since the sol-gel reactions previously performed at TPL involved far less acid catalysis, it was suspected that excess acid might be detrimental. Therefore, it was considered desirable to neutralize some of the HI produced by the iodine oxidation.

$$2 \text{ R-S-H} + \text{I}_2 + \text{Base} \longrightarrow \text{R-S-S-R} + \text{H-Base}^+ \text{ I}^-$$
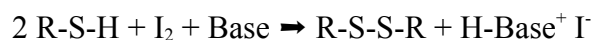
It was decided to combine the TMSi-SH with the desired amount of tetraethoxysilane, (TEOS), a silica precursor, prior to iodine treatment. Similarly, in preparation for the sol-gel hydrolysis and condensation, which are conducted in ethanol, ethanol was used as solvent for iodine oxidation. Two basic choices for neutralization are possible: one generating an iodide salt that is soluble in ethanol (*e.g.* NH$_3$, yielding soluble NH$_4$I), or one generating an insoluble iodide salt (*e.g.* KOH, yielding slightly soluble KI). It was thought that the presence or absence of a soluble salt might affect the polarity of the solution, and thus influence the sol-gel reaction, its product, and its processing.

In a preliminary experiment, TMSi-SH was dissolved in ethanol in a small beaker, open to the air. Iodine crystals were added; they soon formed a dark brown liquid phase on the bottom. Upon swirling, the brown phase quickly dissipated, leaving a uniformly clear colorless solution. This indicated that the oxidation of thiol groups by iodine proceeds rapidly.

To determine how best to conduct the oxidation of TMSi-SH, a 1:3 molar ratio of TMSi-

SH to TEOS was dissolved in enough dry ethanol to make a solution containing 1.0 moles of silicon per liter. An amount of iodine sufficient to oxidize half of the thiol groups was added, followed by addition of an ethanol solution of base. After neutralization, the solution was filtered, if it contained a KI precipitate. Then, the general sol-gel process, discussed in depth in the following section, was conducted to produce a solid silicate. A series of experiments following this general protocol indicated no significant difference between neutralization with either KOH or concentrated aqueous ammonia. Amount of base added was varied so that the resulting alcoxide-to-acid ratio was either 2.0 or 0.6; gels with either ratio gelled equally well. In some runs, the iodine and neutralizing base were added in several small portions, while in other runs, all iodine was added at once, followed by addition of all base after all iodine color had vanished. Subsequent gelation was equally effective, regardless of how the iodine and base were added.

Plackett-Burman experiments indicated that I:S ratios most strongly affect gel time, with high I:S ratios gelling more rapidly. We have observed in previous work that highly polar organic groups lead to slower gelation. Since iodine converts two fairly polar thiol groups to one less-polar disulfide linkage, it is reasonable that increasing the I:S ratio would speed gelation.

4.1.2   Sol-gel Hydrolysis

Sol-gel chemistry is the process of creating solid matrices from liquid or suspended precursors. It typically forms X-O-X bonds, where the O is an oxygen atom and the X's can be silicon or another metal atom. Reaction conditions can be adjusted to produce dense glasses or porous solids, in a great variety of shapes.

The chemistry of a sol-gel process is normally composed of two reactions. The first is a hydrolysis reaction which activates the silica by creating reactive hydroxyl groups on a silicon atom. The starting material is typically a silicon alkoxide, most commonly tetraethoxysiliane (TEOS, or tetraethyl orthosilicate) or tetramethoxysilane (TMOS). The second is a condensation between hydroxyl groups on two silicon atoms to form a siloxane bond and a water molecule. In TPL's ultraporous silica chemistry, the reaction scheme is:

Hydrolysis

Condensation

As more siloxane bonds form, a network develops which eventually gels into a solid material.

The reaction conditions can be modified by amount of acid or base catalyst,

concentration, temperature, solvent and reaction time to create a wide variety of final products. Post-processing and drying techniques can further modify the physical characteristics of the product, producing a range of materials from ultralight aerogels with surface areas above 800 m^2 per gram to dense, clear monoliths of minimal porosity.

Silanes can be obtained with a great many modifying groups. This allows one to greatly modify the final properties of the silica with near-perfect homogeneity. The 3-mercaptopropyl groups used to bind mercury atoms and ions are incorporated into the silicate by substitution of 3-mercaptopropyl trimethoxysilane (TMSi-SH) for some of the TEOS.

Initial experiments attempted to synthesize T-450, the material in which all thiol groups were oxidized by iodine, prior to sol-gel processing. It was found that gelation occurred too rapidly. This was at first attributed to allowing too much time for condensation of hydrolyzed TEOS and TMSi-SH. When reaction time was reduced to one minute, though, gelation still occurred too rapidly to permit pouring into suitable molds. It was next hypothesized that the rapid condensation was a consequence of the highly non-polar nature of the reactants: the unoxidized mercaptopropyl group contains a highly polar S-H bond, which oxidation converts to a non-polar S-S bond. Addition of unoxidized TMSi-SH to the mixture of TEOS and oxidized TMSi-SH was thought to increase polarity of the reaction mixture, thereby slowing condensation, and ultimately yielding practical gelation times. Synthesis of this hybrid material (containing both the unoxidized mercaptan groups of T-350 and the oxidized disulfide groups of T-450) did in fact proceed smoothly, with a gelation time of approximately 30 seconds.

Plackett-Burman analyses of gelation times and mercury adsorption were then conducted separately. The most important factors influencing mercury adsorption were method of removal of ethanol and amount of water used for hydrolysis; evaporating ethanol without water treatment, and the higher water-to-alkoxide ratio, were significantly more effective ($p = 0.05$). Reaction time data indicated that longer reaction time and higher water-to-alkoxide ratio significantly reduced gelation time ($p = 0.05$). Although not significant at $p = 0.05$ confidence levels, the data strongly suggested that room-temperature reaction yielded a product with higher Hg adsorption than 50 °C reaction, and that rapid addition of iodine, followed by rapid addition of base, causes faster gelation than bit-by-bit addition. The data leaned slightly toward the lower alkoxide-to-acid ratio (60) causing higher Hg adsorption and faster gelation, relative to the higher ratio (144); likewise, the data hinted that KOH might give slightly better Hg adsorption and faster gelation than NH$_3$. Since the gelation times experienced thus far had been slower than ideal, and since higher Hg adsorption is always preferable, it was decided that future reactions would employ rapid addition of iodine followed by rapid addition of fairly high amounts of NH$_3$ to reduce HI concentrations to relatively low alkoxide-to-acid ratios. Then, a relatively large amount of water would be added, followed by fairly long reaction times at room temperature.

The choice of NH$_3$ or KOH to neutralize the excess HI had little effect on gelation time. The nature of the base was of interest, because neutralization with ammonia generates ammonium iodide, which is highly soluble in ethanol, while use of KOH generates KI, which is much less soluble, and can be filtered out of the reaction. It was thought that presence of a salt might have an effect on the polarity of the reaction medium, and therefore on reaction time and outcome. Evidently, this hypothesis is not true. As described in the previous section, the amount of base used, which determines the amount of HI remaining to catalyze the hydrolysis, is of little significance. Likewise, the method of addition of base is of little significance: adding all of the iodine to the TMSi-SH/TEOS mixture, followed by addition of all base, is comparable to alternate addition of small portions of iodine and base.

A series of experiments was then conducted to narrow down the optimal amount of water, density, and method of rinsing the finished gels. To increase capacity for mercury, as well as to reduce gelation time, the sulfur-to-silicon ratio was increased to 0.333, and the iodine-to-sulfur ratio was increased to 0.667 in these reactions. Acid-to-alkoxide ratio was maintained at 60. Water-to-alkoxide ratio was evaluated by synthesizing gels with H$_2$O:RO = 1.5, 2.5, and 3.5, while holding [Si] constant at 1.0. The effect of density was studied by producing gels with [Si] = 1.0, 0.8, 0.65, and 0.5, holding H$_2$O:RO constant at 2.5. These gels were each washed three times with ethanol, prior to drying overnight at 67 °C. The effect of additional washing of gels with ethanol was evaluated from four gels, each made with [Si] = 1.0 and H$_2$O:RO = 2.5. One was not washed, one was washed once, one washed twice, and one washed three times, each with 100 mL of fresh ethanol. The fourth washing was after breaking up the gel into small pieces; all other washings on all gels were with the gel an intact disc. All samples were briefly left in the hood for some ethanol to evaporate, and then placed in a ventilated drying oven at 67 °C overnight. Dried samples were further broken up, and sieved through 10-, 18-, and 45-mesh sieves. Samples weighing approximately 0.3 g of the 10-18 mesh fractions were placed in 50-mL beakers, in a desiccator with an open bottle of mercury, for two days.

Results indicated that increasing water to 3.5 moles per mole of alkoxide yields superior Hg adsorption, relative to 1.5 or 2.5 molar ratios. Washing the gels is important; the unwashed gel had markedly lower Hg adsorption, while the most-washed gel was markedly improved. Silicon concentration had little effect. This is most likely due to partial collapse of the porous structure, so that all gels were comparably porous.

All of the preparations tested thus far adsorbed far less than their theoretical capacity. Since higher porosity could potentially increase availability of disulfide linkages to mercury atoms, it was desirable to produce gels with reduced density. Initial attempts to produce silicates with low density employed completely oxidized TMSi-SH, and fairly long refluxing times;

products coagulated very rapidly, and had poor homogeneity. Later attempts, with 50% of the TMSi-SH oxidized prior to sol-gel reaction, yielded very slowly gelling products, with poor homogeneity. Other formulations with low density gelled satisfactorily, but in the drying stage, they collapsed into higher density solids. It was then hypothesized that reducing the polarity of the organic group, by increasing the proportion of silicon atoms containing nonpolar groups, might yield stronger more porous gels. A first attempt used oxidized TMSi-SH in much higher amounts than previously used. Six formulations were produced, all with S:Si = 0.5, I:S = 0.7, RO:H$^+$ = 60, and H$_2$O:RO = 3.5. Two had [Si] = 1.2 M, two had [Si] = 0.70, and two had [Si] = 0.49. They were tested alongside two previously synthesized "control" gels with [Si] = 1.0, S:Si = 0.33. and I:S = 0.67. The six gels with higher S:Si and I:S gels were thought likely to have higher Hg adsorption than the controls, but experimental results showed comparable Hg adsorption after two days exposure.

Since S:Si ratios of 0.5 and 0.33 had comparable Hg adsorption, the lower S:Si ratio would be more desirable, because the reagent supplying sulfur is considerably more expensive than the other silicon-containing materials. Therefore, it was desirable to determine how low S:Si could be taken, without adversely affecting product quality. A Plackett-Burman experiment testing S:Si = 0.05 *vs.* S:Si = 0.10 was conducted, with the products tested against each other, as well as against the two best-adsorbing samples from previous Plackett-Burman experiments, each with S:Si = 0.33. Results showed that S:Si = 0.05 was slightly more effective than S:Si = 0.10, and almost all S:Si = 0.05 and S:Si = 0.10 samples were more effective than the S:Si = 0.33 samples. It must be pointed out that other parameters were different between the samples, so the apparently lower performance of the 0.33 samples was probably due to some of these other factors. Nevertheless, it is clear that reducing S:Si to 0.05 does not significantly reduce performance.

4.1.3   Gelation of the Sol
This step proved to be the least critical to the performance of product. Addition of concentrated aqueous ammonia raised the pH to 8-11; the high buffering ability of ammonia means that achieving this pH range is straightforward. Within several minutes, gelation occurs. The time of gelation depends largely on the extent of hydrolysis; sols gelling within 1-2 minutes seem to have more mechanical stability. Such a gel time can be achieved by adjustment of parameters, most particularly time and temperature of hydrolysis.

4.1.4   Final Processing: Washing, Drying, and Sizing the Solid Material
It was found to be much easier to use T-450 as a particulate material, rather than forming it into thin membranes. Indeed, the word "membrane" is not appropriate for this application, since mercury is adsorbed on the material rather than separated on one side of the membrane. So, to achieve the goal of development and use of a material to remove Hg vapor from gas

streams, it was decided to use a granular form of T-450.

After the sol has gelled, it is allowed to "cure" overnight, by simply remaining immersed in the alcohol-water medium. Several washings in water or ethanol are desirable, by removing ammonium iodide from the silicate. The choice of water or ethanol is not critical to performance of the product, so water was chosen for cost and convenience reasons. The washed gel is dried in a circulating oven overnight at 60 °C, which causes some compaction. Comminution in these laboratory-scale experiments was by mortar and pestle; on a larger scale, a cone mill should be appropriate.

4.2   TASK 2: PHYSICAL AND CHEMICAL PROPERTIES OF THIOL-BASED SOL-GELS

4.2.1   Testing for Elemental Mercury Adsorption

In the Phase I proposal, it was stated that elemental Hg capacity would be tested by placing 1-gram samples of granular material in a sealed desiccator containing an open dish of liquid mercury. After one week, it was envisioned that the sample would be removed and "wet-ashed" with concentrated aqueous nitric acid. The extract would be analyzed for Hg content by atomic absorption (AA) spectrometry, using a Perkin-Elmer cold-vapor mercury apparatus. It was unknown how rapidly T-450 would adsorb mercury; one week was thought to be long enough to adsorb measurable quantities. Similarly, it was unknown how particle size would affect Hg absorption. Early experiments demonstrated that exposure of quarter-gram samples to Hg for two days was sufficient to measure Hg adsorption, and that particle size was not important: 10-18 mesh T-450 was no different than 18-45 mesh.

Since the vapor pressure of Hg at 20 °C is 1.2 torr, air saturated with mercury contains 12.9 μg of Hg per liter of air. The heat of vaporization of mercury at its boiling point is 59.1 kJ/mol, or 294 J/g; it can be assumed that it is comparable at room temperature. Heat capacity at constant pressure is 28.00 J/mol.K, or 0.140 J/g. If 10 grams of material adsorb at a rate of 6 μg/hr.g, then total Hg absorption is 60 μg/hr. This requires 0.0176 J/hr to evaporate Hg. This low amount of energy indicates that the air in the chamber will easily remain saturated with Hg.

4.2.2   Resistance to Acidic Atmosphere

Two samples of T-450, each having S:Si = 0.33, I/S = 0.67, [Si] = 1.0 M, [RO]:H$^+$ = 60, and particle size 18-45 mesh, were selected for testing for durability under moist acidic conditions. The samples differed only in [H$_2$O]:[RO], having ratios 2.5 and 3.5. As a control, 20-40-mesh Darco activated carbon was used. For each of the three materials, three 0.25-g samples were placed in a 9.5-L desiccator containing 2.0 mL of conc. aq. HCl. The desiccator was partially evacuated, and placed in a 70 °C drying oven for 15.5 hours. The desiccator was

then opened, and all samples were allowed to air and dry out at 70 °C for one hour in the drying oven. The nine samples, joined by two samples of each material that had not been exposed to HCl, were then sealed in a container containing an open bottle of elemental Hg, at room temperature, for 113 hours. The fifteen samples were wet-ashed with double-distilled conc. aq. HNO₃, and extracts analyzed for Hg content. Results are tabulated below.

	Treated with HCl (n = 3)	Not treated with HCl (n = 2)
T-450, formula A	0.139 µg/g	0.054 µg/g
T-450, formula B	0.095	0.030
Activated carbon	0.057	0.033

These results indicate that exposure to warm HCl does not impair Hg adsorption; if anything, it improves it. It also demonstrates that under hot acidic conditions, only 41 grams of T-450 is as effective as 100 g of activated carbon.

4.2.3   Porosimetry Tests

Nitrogen physisorption studies were performed with the Brunauer-Emmett-Teller (BET) gas adsorption method on a Micromeritics ASAP 2010 porosimeter. A 0.1628-g granular sample of the T-450 used in the Task 4 tests was found to have a surface area of 826.3 ± 1.7 m^2/g and a pore volume of 0.524 cm^3/g.   From the surface area, SA, and pore volume, V, assumption of cylindrical pores enables calculation of a mean hydraulic diameter d, from the equation $d = 4V/SA$. Thus, the mean hydraulic diameter is 2.54 nm. The size of a gaseous atom is an ill-defined quantity, but the atomic radius of crystalline mercury is 0.151 nm (*Lange's Handbook of Chemistry*, 14th edition, pg. 4.14). Assuming that this is a reasonable approximation to a gaseous atom leads to the conclusion that the mean hydraulic diameter of T-450 is about 8-fold larger than the diameter of a mercury atom. Thus, a mercury atom should be able to travel through the pores, even after the pore size has been reduced by binding other mercury atoms. This is consistent with the finding that, for a given formulation of T-450, coarse and fine particles are equally effective at Hg adsorption: the inside of a particle is as accessible to Hg as the outside.

4.2.4   Adsorption of Ionic Mercury

Although the primary difficulty in removing Hg from flue gases is with elemental mercury, it is also desirable to know how effective TPL materials can be for adsorbing Hg (II) compounds. In flue gases (especially in incinerators burning chlorinated polymers), mercury (II) is most commonly found as HgCl₂, a largely covalent compound with m.p. 280 °C and b.p. 303 °C.[iii] Although it would be desirable to study HgCl₂ vapor, this is beyond the scope of the Phase I program. General information will be obtained from a much simpler system, aqueous HgCl₂.

Three quarter-gram samples each of granulated T-350 and T-450 were placed in 20-mL polyethylene vials, and treated with 10-mL aliquots of 2.82 mM aqueous Hg(NO₃)₂ (5.64 g

Hg/L). After brief gentle agitation, the samples sat undisturbed for two hours, and a sample of supernatant solution was drawn analyzed for Hg by flame AA. The Hg^{2+} capacity of T-350 was 0.2031 g Hg/g, and of T-450, 0.0410 g Hg/g.

The sample of T-450 had S:Si = 0.05, and I:S = 0.9. This combination of low sulfur concentration and high iodine concentration means that the ratio of unoxidized thiol groups to silicon atoms was only 0.005. Assuming that only unoxidized thiol groups can bind Hg^{2+}, and that two thiol bind one Hg^{2+} leads to a theoretical capacity of 0.0077 g Hg/g. Since the observed capacity was more than five-fold greater, it must be concluded that even oxidized disulfide linkages have some ability to bind Hg^{2+}. Thus, even formulations of T-450 that are designed only for elemental mercury are also effective at removing ionic mercury from flue gases. This is especially significant for applications such as waste incineration, in which a substantial fraction of mercury is ionic.

4.3   TASK 3: INDUSTRIAL APPLICATIONS

To best determine which T-350 and T-450 formulations are most suitable for further testing beyond the basic tests of Task 2, data on actual industrial applications are needed. TPL therefore contacted Mr. Joe H. Tallon, an environmental engineer for Santee Cooper, the South Carolina public service authority. Santee Cooper is a state-owned utility that serves 126,000 direct customers in three counties, generates power for 15 of the state's 20 electric cooperatives serving 437,000 customers in 38 counties, and directly serves 34 industrial customers in 11 counties. Santee Cooper operates four coal-fired plants in South Carolina. Mr. Tallon stated that the suggested activated carbon technology fails to completely solve the problem, in that it converts mercury contamination in air into mercury contamination in fly ash. When informed that T-450 could be used in much larger particle sizes that could be captured before entering the particulate control system, he expressed that this would be desirable, because it would enable collection of a much-more concentrated mercury contaminant, from which Hg recovery and recycling might be feasible.

4.4   TASK 4: TESTING UNDER FLUE GAS CONDITIONS

It is necessary to test operation of a new material under conditions more closely matching actual industrial use conditions. In TPL's Phase I proposal, the apparatus was suggested for testing T-450 under conditions mimicking a rudimentary flue gas system; with slight modification such a system was constructed. The photograph on the left illustrates the entire system. All of the apparatus was contained in a ventilation hood. The main modification in this scheme was the replacement of disks with a series of two columns containing granular 10-20 mesh material. The columns consisted of 3" long pieces of ½" iron pipe (black, not galvanized,

since the zinc coating would react with Hg), with inside diameter of 0.622", and are shown in the photograph above. Each column was fitted on both ends with a ½" to ⅛" reducer; the reducers held a disc of 100-mesh stainless steel screen, to contain the granular T-450 sample. Short nipples of ⅛" pipe were attached to the reducers, to enable connection to ⅛" i.d. silicone hose. Each column could contain up to 7.5 g of T-450, or 4.5 g of Darco 20-40-mesh activated carbon. Elemental Hg vapor was generated in a Perkin-Elmer cold vapor apparatus, designed to convert aqueous Hg (II) salts to Hg vapor for analysis in an AA spectrometer. One-mL aliquots of a commercially-prepared Hg standard (1 mg of Hg per mL, in 1% aq. HNO_3) were placed in the generator flask. When ready to generate Hg vapor, the operator activates a switch that adds an excess of a reductant solution, alkaline sodium borohydride. Hydrogen, produced by the reaction of borohydride and acid, moves the Hg through silicone rubber tubing into the oven, to the columns containing T-450. The tubing was coiled such that gas entering the columns was heated to 100 °C. Any Hg vapor passing through the membranes would leave the oven and be bubbled through a nitric acid/potassium permanganate solution in the trap; this converted it to non-volatile aqueous Hg (II), thereby preventing its escape into the atmosphere. After each 1-mg aliquot of Hg was added to the system, the trap solution was removed, and replaced with a fresh trapping solution. After six aliquots were added, the column was opened, and the contained T-450 or carbon was wet-ashed for analysis by cold-vapor Hg AA. Samples of each trapping solution were also analyzed for Hg content.

In a preliminary experiment, six 0.1 mg Hg injections were made; with T-450, all 0.6 mg of Hg was collected in the first column, with none observed in the second column or trapping solutions. Activated carbon collected 0.09 mg Hg in the first column, and none in the second column or trapping solutions.

Next, six 1.0-mg Hg injections were made, with two fresh columns of T-450 or activated carbon. T-450 adsorbed 0.18 mg in the first column, and none in the second; activated carbon adsorbed 0.135 mg in the first column, and 0.014 mg in the second column. The trapping solutions from each sorbent contained no measurable Hg.

These results defy simple interpretation. The experimental difficulties explained below suggest that these data should be regarded only as indicating general trends, and not quantitative conclusions.   Most important to note is that one column of T-450 removed all mercury passing through it: none was present in the second column. Activated carbon was less successful, with 10% of the mercury entering the first column passing through to the second.

These measurements were fraught with difficulty, due to the nature of the source of mercury vapor. The Perkin-Elmer cold vapor device was designed to convert ionic Hg in acidic solutions into Hg°, which is blown by hydrogen to the spectrometer. Nitrogen is used mainly to

push the reductant solution into the sample vessel; it provides very little gas flow from the generator, contrary to the assumption made in devising this experiment. To have adequate gas flow into the columns in the oven required an auxiliary source of nitrogen; this connection resulted in a significant unavoidable loss of mercury from the apparatus. By using the same device for production of mercury for the columns (1 mg per injection) as well as for its designed purpose, analysis of aqueous solutions resulting from it (*ca.* 0.2 μg and less per analysis), the possibility of contamination of the apparatus exists. Furthermore, the system was different from flue gas conditions in at least two major ways. First, the presence of large amounts of hydrogen made the system strongly reducing, instead of the atmosphere of combustion, which still contains significant amounts of oxygen, and much lower amounts of reducing gases. Second, the mercury was supplied in large bursts, instead of the steady stream of low Hg emitted from a power plant.

A modification of this system was then constructed, so that an aqueous Hg^{2+} solution was slowly and uniformly pumped into an alkaline sodium borohydride solution. First, the Hg from 10 mL of 0.1% Hg^{2+} solution (10 mg Hg) was applied to three columns each containing 4.5 g of T-450; the first column captured 0.378 mg of Hg, with none observed in the second or third columns, or in the aqueous trap. Then, the process was repeated with three columns each containing 4.5 g of Darco activated carbon; the first column captured 0.105 mg of Hg, with none observed in the second or third columns, or in the aqueous trap. Although the T-450 was 3.6-fold more effective in Hg adsorption, it must be noted that most of the Hg was not accounted for, and was apparently lost in the system. Thus, these results best display trends rather than absolute effectiveness.

For future work, TPL suggests a much more thorough design of a prototype system to evaluate effectiveness of T-450 and competing sorbents, prior to its construction and operation.

4.5 OVERALL EFFECTIVENESS OF T-450 IN CONTROL OF MERCURY CONTAMINATION IN FLUE GASES

TPL envisions that use of T-450 will be compatible with conventional emission control systems presently used in coal-fired power plants. At this time, TPL is assuming that the best solution is addition of a mercury sorbent to the flue gas; activated carbon is the most commonly considered sorbent. For T-450 to be superior to activated carbon requires not that its cost be less than the very low cost of activated carbon, but rather the cost of *using* T-450 be less than the cost of *using* activated carbon. Since there are currently no regulations regarding mercury emissions from power plants, any system will involve significant changes to the current emission control system. It is likely that the cost of the sorbent will be a small fraction of the cost of the equipment to implement it. Therefore, the preferred sorbent will win out based on the cost of the newly-required equipment necessary to utilize it. T-450's advantage is that its higher affinity for

mercury will mean much smaller equipment will be necessary to apply it. This cost savings will more than exceed any premium paid per pound of sorbent.

Since there are no current U.S power plants using any system for reducing mercury from their emissions, it is difficult to state exactly how much less equipment costs would be for using T-450. However, chemical engineers use some rules of thumb for estimating equipment costs versus capacity. *Perry's Handbook of Chemical Engineering*,[iv] 7th ed., shows that, for example, an x-fold increase in capacity of an electrostatic precipitator results in an $x^{0.81}$-fold increase in cost, while an x-fold increase in capacity of a shaker-type cloth dust collector results in an $x^{0.79}$-fold increase in cost. Flowing air tests indicated that use of activated carbon instead of T-450 means a 3.6-fold increase in mass of sorbent. Assuming then this factor of 3.6 for equipment sizing, and an exponent of 0.8, indicates that the equipment required for activated carbon use would cost 2.79 times the cost of the same equipment sized for T-450. For purposes of estimating, we speculate that the cost of reducing Hg emissions from coal-fired power plants using activated carbon is 3% cost of sorbent, 75% cost of size-sensitive equipment, and 22% cost of labor and non-size-sensitive equipment. Then it can be shown that the savings in equipment cost by using T-450 is equal to a price ratio of 17; in other words, if T-450 use means 3.6-fold less sorbent required, and T-450 costs 17-fold more than the cost of activated carbon, then use of the two materials has equal cost.

Therefore, the cost of production of T-450 must be estimated. A more thorough estimate is possible only after operation of a pilot plant. At this time, however, a preliminary estimate can be made. For this exercise, we will use the composition used in the Task 4 testing: S:Si = 0.05, Me:Si = 0.25; and I:S = 0.9. The total cost of the four consumed materials (3-mercaptopropyl trimethoxysilane, methyl trimethoxysilane, tetraethoxy orthosilicate, and iodine), for barrel-sized quantities, is $9.57 per pound of T-450 produced. If ethanol is not recovered and recycled, its cost adds $1.34 to the cost of a pound of T-450; savings through recycling are likely. For sol-gel silicates, an initial estimate for other production costs (including labor and equipment) is 100% of material costs; pilot plant operation will yield a more accurate figure. Thus, without ethanol recycling, the estimated cost of producing T-450 is $21.82 per pound; a lower cost might be possible.

The activated carbon that TPL used as a comparison to T-450 was Darco 20-40 mesh, which costs $2.37 per pound. The cost premium of T-450 is only 9.2-fold over the cost of Darco, much less than the break-even ratio of 17 calculated above. Using the 9.2-fold ratio for price premium indicates that the total cost of Hg removal is 23.5% less with T-450 than with Darco activated carbon. However, the savings could be much greater: activated carbon suffers from poor consistency, with high Hg removal rates in some plants and much lower rates in others. The high selectivity of T-450 makes it unlikely to suffer from loss of performance as conditions

change.

For these reasons, there is an excellent chance that T-450 is the more economical sorbent for mercury in flue gas of coal-fired power plants. Future research and development is necessary to determine more accurately the benefits of its application.

5. ACCOMPLISHMENTS AND CONCLUSIONS

All Phase I objectives were met. TPL has synthesized, by sol-gel methods, a silicate with high affinity for elemental mercury and ionic mercury. It was found to be superior to activated carbon in adsorbing Hg vapor from air. The feasibility of its use in flue gas cleanup was evaluated, and found to be favorable.

The following results were obtained:
1.	Feasibility of synthesizing an organically modified silicate with disulfide linkages was demonstrated.
2.	Several synthetic methods were evaluated, and the product properties resulting were determined. A material was found that combined porosity, strength, ease of production, and high affinity for both elemental and ionic mercury.
3.	Comparison with activated carbon indicated a 3.6-fold increase in mercury adsorption, relative to activated carbon
4.	The cost of full-scale production was estimated to be $22 per pound.
5.	Economic analysis indicated that use of T-450 instead of activated carbon will enable dramatic savings in cost of equipment. This is projected to result in a savings of 23.5%, relative to use of activated carbon.

6. RECOMMENDATIONS

TPL believes the results of the Phase I program warrant further research and development.

TPL has demonstrated that T-450 offers a dramatic improvement over the state of the art, both in terms of cost and performance, for clean-up of mercury-containing flue gas. The proposed Phase II work will scale up both the synthesis of T-450, and the testing of T-450 in situations of industrial interest. This will yield data both on the cost of full-scale production of T-450, and on the performance to be attained in industrial applications.

Given the EPA estimate of $5 billion per year to meet possible mercury emission standards for coal-fired power plants, the projected savings indicated by TPL's Phase I results makes future research and development highly warranted.

7. REFERENCES

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