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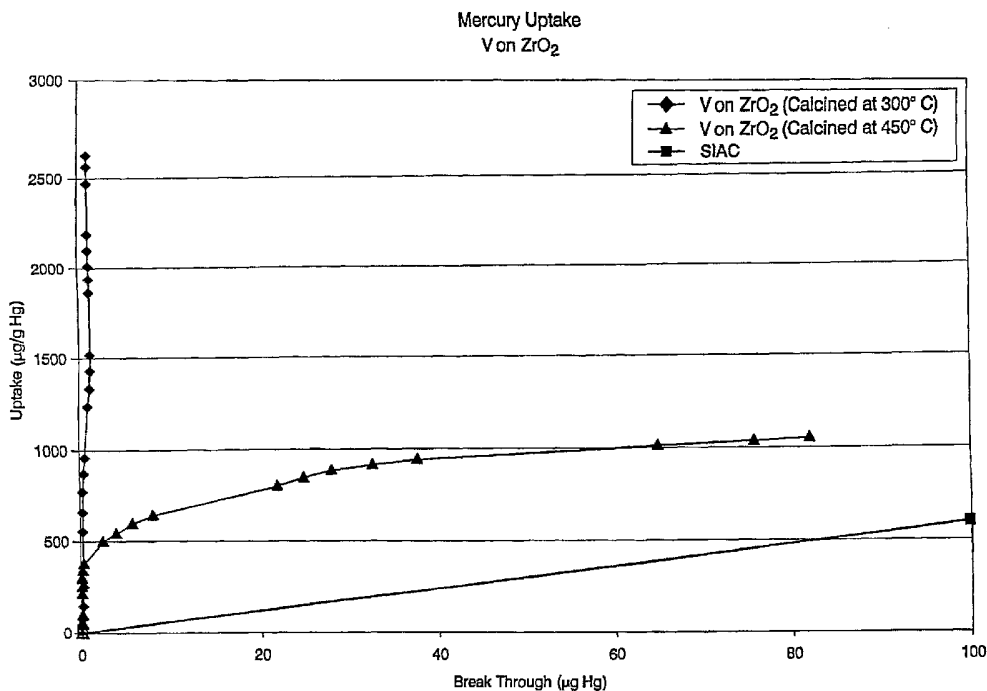
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(54) **Title:** MERCURY REMOVAL SORBENT



(57) **Abstract:** A sorbent composition comprising a vanadium compound and a ZrO₂ support material is disclosed. Methods of making and using the composition to remove heavy metals or heavy metal containing compounds from a fluid stream are also provided. Such methods are particularly useful in the removal of mercury and mercury compounds from flue gas streams produced from the combustion of hydrocarbon-containing materials such as coal and petroleum fuels.

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MERCURY REMOVAL SORBENT

The invention relates to a composition and method for removing heavy metal contaminants from fluid streams. In one aspect, the invention relates to a composition for sorbing heavy metal contaminants and a method of preparing such composition. In yet
5 another aspect, the invention relates to a process for removing heavy metal contaminants, such as mercury and mercury compounds, from flue gas streams produced from the combustion of hydrocarbon-containing materials.

When used herein the phrases "consists essentially of", "consisting essentially of" and similar phrases do not exclude the presence of other steps, elements,
10 or materials that are not specifically mentioned in this specification, as long as such steps, elements or materials, do not affect the basic and novel characteristics of the invention, additionally, they do not exclude impurities normally associated with the elements and materials used.

The above terms and phrases are intended for use in areas outside of U.S.
15 jurisdiction. Within the U.S. jurisdiction the above terms and phrases are to be applied as they are construed by U.S. courts and the U.S. Patent Office.

Heavy metals are released during the combustion process of many fossil fuels and/or waste materials. These heavy metals include, for example, arsenic, beryllium, lead, cadmium, chromium, nickel, zinc, mercury, and barium. Most of these
20 heavy metals are toxic to humans and animals. In particular, elemental mercury and mercury compounds such as mercury chlorides are thought to compromise the health and mental acuity of young children and fetuses.

Furthermore, there is every indication that the amount of mercury, and possibly of other heavy metals, now legally allowed to be released by those combusting
25 various fossil fuels and/or waste materials, including coal burning powerplants and petroleum refineries, will be reduced by future legislation. While a variety of adsorbents are available for capture of heavy metals (in particular mercury), these adsorbents tend to have low capacities and are easily deactivated by other components in the gas stream, such as sulfur oxides. Thus, there exists a need for a material that removes elemental

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mercury from gas streams and has a high capacity for retaining mercury as a nonvolatile compound.

It is desirable to provide an improved vanadium material with a high capacity for sorbing heavy metals and heavy metal compounds.

5 Again it is desirable to provide a method for making an improved vanadium incorporated sorbent material by incorporating a vanadium-containing compound with a porous support material.

 Once again it is desirable to provide a process for removing heavy metals or heavy metal compounds from a fluid stream by contacting the fluid stream with an
10 improved vanadium incorporated sorbent material.

 Again it is desirable to provide an improved vanadium material which when used in the removal of heavy metals results in the oxidation of the heavy metal to an oxidation state greater than zero.

 It should be understood that the above-listed desires are only exemplary,
15 and not all the desires listed above need be accomplished by the invention described and claimed herein.

 In accordance with a first embodiment of the invention, the inventive composition comprises particles of a ZrO_2 support having incorporated onto, into, or onto and into at least one source of vanadium selected from the group consisting of
20 vanadate ions, vanadium oxide, and combinations thereof, the material comprising at least about 5% by weight vanadium. In accordance with a second embodiment of the invention, the inventive composition is prepared by a method comprising the steps of:
(a) incorporating into, onto, or into and onto a porous ZrO_2 support a mixture including a source of vanadate ions, and a solvent capable of solubilizing said source of vanadate
25 ions; (b) drying the vanadate incorporated ZrO_2 material; and (c) calcining the dried vanadium incorporated ZrO_2 material.

 In accordance with a third embodiment of the invention, the inventive composition is prepared by a method comprising the steps of: (a) preparing a mixture

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comprising a source of vanadate ions and a solvent capable of solubilizing the source of vanadate ions; (b) adding a quantity of an oxidizing agent to the mixture; (c) intimately mixing the mixture with a quantity of ZrO_2 particles; (d) drying the intimate mixture thereby forming a vanadium incorporated ZrO_2 material; and (e) calcining the vanadium incorporated ZrO_2 material.

In accordance with a fourth embodiment of the invention, the inventive composition can be used in the removal of at least one heavy metal or heavy metal containing compound from a fluid stream by a method comprising the step of: (a) contacting the fluid stream with a porous ZrO_2 support material having incorporated onto, into, or onto and into a vanadium containing compound for sorption of at least a portion of the at least one heavy metal or heavy metal containing compound.

In accordance with a fifth embodiment of the invention, the inventive composition can be used in the removal of at least one heavy metal or heavy metal containing compound from a flue gas stream produced by the combustion of a hydrocarbon-containing fuel, the method comprising the steps of: (a) contacting the flue gas stream with a first sorbent material comprising a porous ZrO_2 support material having incorporated onto, into, or onto and into a vanadium containing compound for sorbing at least a portion of the at least one heavy metal or heavy metal containing compound present in the flue gas stream; and (b) contacting the flue gas with a second sorbent material different from the first sorbent material for sorbing at least a portion of the at least one heavy metal-containing compound not sorbed during step (a). Other objects and advantages of the invention will become apparent from the detailed description and the appended claims.

A preferred embodiment of the present invention is described in detail below with reference to the attached figures, wherein:

FIG. 1 is a graph of mercury uptake versus mercury breakthrough for a vanadium incorporated ZrO_2 sorbent compared to a conventional activated charcoal sorbent; and

FIG. 2 is a graph of the mercury removal efficiency for a vanadium

incorporated ZrO₂ sorbent.

Compositions according to the present invention generally comprise a porous ZrO₂ support material having incorporated thereon, therein, or thereon and therein a vanadium-containing compound. Preferably, the vanadium compound is any such compound wherein the vanadium component is in a +5 oxidation state. Preferably, the vanadium-containing compound comprises a vanadium oxide, more preferably V₂O₅ or a vanadate (-VO₃) group, such as in ammonium vanadate (NH₄VO₃). However, it is within the scope of the invention for the vanadium component to have any oxidation state greater than zero.

The porous ZrO₂ support material generally comprises at least about 50% by weight of the total composition, preferably between about 50-99% by weight, more preferably between about 75-95% by weight, and most preferably between about 80-90% by weight. In order to maximize the sorptive capacity of the composition, the support material preferably has a surface area of at least about 75 m²/g, more preferably at least about 100 m²/g, and most preferably at least about 150 m²/g.

The overall composition comprises at least about 5% by weight vanadium. Unless otherwise specified, the phrase "by weight vanadium" is defined as the elemental weight of vanadium present in the composition. More preferably, the composition comprises from about 7-40% by weight vanadium, and most preferably from about 10-25% by weight.

In one embodiment, the sorbent material is formed by incorporating into, onto, or into and onto a porous ZrO₂ support a mixture including a source of vanadate ions, a solvent capable of solubilizing the source of vanadate ions, and an oxidizing agent. Preferably, the source of vanadate ions is NH₄VO₃, however, other sources of vanadate ions such as alkali metal vanadates may be used. As noted above, it is preferable for the vanadium present in the vanadate ions to have a +5 oxidation state. The selection of the solvent for solubilizing the vanadium-containing compound is important in achieving this objective. However, it is also preferable to add an oxidizing agent to the mixture to ensure that the vanadium maintains a +5 oxidation state. In this regard, preferred solvents for use with the present invention include those selected from

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the group consisting of oxalic acid, HNO₃, HCl, and mixtures thereof, with oxalic acid being particularly preferred. Preferred oxidizing agents for use with the present invention include those selected from the group consisting of H₂SO₄, HNO₃, permanganate, ozone, H₂O₂, and mixtures thereof, with H₂O₂ being particularly preferred. Preferably, the oxidizing agent is added in a sufficient quantity so as to maintain the vanadium present in the vanadate ions in a +5 oxidation state, more preferably, this involves the presence of about 0.1-25% by weight oxidizing agent based on the weight of the vanadate solution, and most preferably from about 1-10% by weight. It is possible for a single material to act as both a solvent and oxidizing agent, however, it is most preferable for the oxidizing agent to be a composition different from the solvent. When preparing small batches of sorbent material in accordance with the present invention, it is preferable for the oxidizing agent to be added to the vanadate solution slowly, and more preferably in a drop wise manner.

Next, the vanadate mixture is combined with a quantity of ZrO₂ particles thereby forming a vanadium incorporated ZrO₂ material. The ZrO₂ particles can be discrete granular particles or agglomerations of a plurality of particles. Preferably, the ZrO₂ particles or particle agglomerations have an average particle size of between about 0.01-20 mm, more preferably from about 0.1-10 mm, and most preferably from about 0.5-5 mm. It is preferable that the ZrO₂ particles not be in the form of a powder, however, it is possible for a powder to be used provided that the powder can be formed into pellets or other larger granular structures.

In preferred embodiments, the vanadate mixture is intimately mixed with the ZrO₂ particles so that at least a portion of the vanadate ions impregnate the ZrO₂ support. By impregnating the pores of the support material, the surface area available for heavy metal sorption is significantly increased. As used herein, the term "impregnate" means that the vanadate ions at least partially fill in or infuse the pores of the ZrO₂ support.

The vanadium incorporated ZrO₂ material is then dried to remove the excess solvent. Preferably, this drying step involves heating the vanadium incorporated ZrO₂ material to a temperature of at least about 100°C (about 212°F) depending upon

the solvent used. Following removal of the excess solvent, the dried vanadium incorporated ZrO_2 material is calcined. As demonstrated in the examples below, the calcination temperature appears to impact the sorptive capacity of the sorbent material. Therefore, it is preferable that during the calcination step the dried vanadium incorporated ZrO_2 material be heated to a temperature of between about 200 - 600°C (about 392-1112°F), most preferably between about 250 - 450°C (about 482-842°F), and most preferably between about 275 - 375°C (about 527-707°F). During the calcination step, it is possible for at least a portion of the vanadate ions to be converted to a vanadium oxide compound such as V_2O_5 , a hydrate of V_2O_5 , a peroxy complex of vanadium oxide, or mixtures thereof.

The inventive sorbent material is particularly useful in the removal of heavy metals and heavy metal containing compounds from fluid streams, especially flue gas streams produced by the combustion of hydrocarbon-containing materials such as coal and petroleum fuels. As noted above, such fluid streams are often contaminated with at least one heavy metal or compound containing a heavy metal selected from the group consisting of arsenic, beryllium, lead, cadmium, chromium, nickel, zinc, mercury, and barium. In one aspect, methods of removing heavy metal and heavy metal containing compounds from fluid streams comprise providing a sorbent composition according to the present invention and contacting the stream with the inventive sorbent.

Flue gas, such as that created by the combustion of hydrocarbon-containing compounds, generally comprises at least about 10% by weight N_2 , more preferably at least about 50% by weight, and most preferably between about 75-90% by weight. Flue gas also generally comprises less than about 10% by weight of uncombusted hydrocarbons, more preferably less than about 5% by weight, and most preferably less than about 1% by weight. As described below, in a particularly preferred application, the flue gas will have already been treated for removal of NO_x and SO_x prior to any heavy metal removal process as the presence of high levels of NO_x and SO_x compounds may lead to fouling of the heavy metal removal sorbents. Generally, the flue gas comprises less than about 800 ppm of SO_x compounds such as SO_2 , more preferably less than about 500 ppm, and most preferably less than about 400 ppm. Also, the flue gas preferably comprises less than about 400 ppm NO_x such as NO and NO_2 ,

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more preferably less than about 250 ppm, and most preferably less than about 150 ppm. Flue gas may also comprise between about 2.5-10% by weight O₂, between about 1-5% by weight CO₂, and between about 5-20% by weight H₂O.

5 Preferably, the pressure drop associated with the contacting step should not exceed more than about 138 kPa (about 20 psia). More preferably, the pressure drop in the fluid stream is less than about 69 kPa (about 10 psia), and most preferably less than about 34 kPa (about 5 psia). Typically, flue gas streams do not flow under high pressures. Therefore, if the pressure drop is too great, back pressure is created and can affect the combustion process by which the flue gas is created. The arrangement of the sorbent material in the vessel in which contacting occurs can assist in minimizing this pressure drop. Preferably, the sorbent material comprises finely divided particles that are suspended in the fluid stream during the contacting step. Alternatively, the sorbent material may be positioned in a fluidized bed, placed in a packed bed column, formed into monoliths, or incorporated into a foam. With the latter arrangements, pressure drop 10 may become much more of a concern and may require the use of fans or other equipment to increase the pressure of the flue gas stream.

The fluid stream containing the heavy metal contaminant preferably has a temperature of between about 10 - 204°C (about 50-400°F) during the contacting step, more preferably between about 37.7 - 190°C (about 100-375°F), and most preferably 20 between about 93.3 - 177°C (about 200-350°F). The temperature of the fluid stream at the contacting stage is in part affected by upstream processes such as particulate removal systems (i.e., cyclones), other contaminant removal systems, heat exchange systems, etc. The contacting step results in the sorption of at least about 80% by weight of the heavy metals contained in the fluid stream, more preferably at least about 90% by weight, even 25 more preferably at least about 95% by weight, and most preferably at least about 98% by weight. As previously stated, the vanadium incorporated ZrO₂ support material exhibits a high capacity for sorbing heavy metals and heavy metal containing compounds. Preferably, the vanadium incorporated ZrO₂ material is capable of sorbing at least about 1 atom of a heavy metal per every 5 atoms of vanadium. More preferably, the ratio of 30 heavy metal atoms sorbed to vanadium atoms is at least about 1:3, and most preferably 1:1.

The vanadium incorporated ZrO_2 sorbent material also exhibits the ability to oxidize the elemental heavy metal into a heavy metal containing compound such as a heavy metal oxide or chloride. Using mercury as an example, the sorbent material oxidizes mercury into various oxidized species such as Hg^{+1} , Hg^{+2} , or mercury compounds such as HgO , $HgCl$, and $HgCl_2$. At times, due to system inefficiencies or sorbent saturation, some of these heavy metal containing compounds may desorb or break free from the sorbent material. In that case, it can be particularly useful to employ a downstream heavy metal compound removal system in conjunction with the above-described sorbent system. In the heavy metal compound removal system, the gaseous product stream is contacted with a separate adsorbent in an adsorption zone. The adsorbent can be any adsorbent capable of adsorbing a heavy metal; however, preferred materials for removing the heavy metal compounds include those having a hydrophobic surface with pore openings of less than about 10 Å, and high pore volumes. More preferably, the adsorbent comprises, consists of or consists essentially of a material selected from the group consisting of a zeolite, amorphous carbon and combinations thereof. The amorphous carbon can be an activated carbon and/or activated charcoal. Exemplary zeolites include those with 8-12 member ring openings, and particularly ZSM-5 zeolite. Furthermore, the material may be in the form of granules, pellets, monoliths, powders that are collected on filters, or combinations thereof. A treated gaseous product stream is withdrawn from the adsorption zone and contains less than about 20 weight %, preferably less than about 10 weight %, and more preferably less than about 5 weight % of the heavy metal in the gaseous feed stream.

The heavy metal compound removal system may be contained in a separate downstream vessel from the vanadium incorporated ZrO_2 sorbent, or can be situated along with the vanadium incorporated ZrO_2 sorbent in a multiple stage contacting vessel so that the flue gas first contacts the vanadium incorporated ZrO_2 sorbent followed by the heavy metal compound removal sorbent.

While the vanadium incorporated ZrO_2 sorbent material exhibits a relatively high capacity for sorbing heavy metals and heavy metal containing compounds, its cost is relatively higher than the cost for conventional heavy metal compound sorbent materials such as zeolite. Therefore, from an economic standpoint, it

may be desirable to employ a relatively small amount of the vanadium incorporated ZrO₂ sorbent compared to the conventional sorbent material. Once the sorptive capacity of the vanadium incorporated ZrO₂ sorbent has sufficiently diminished, it will not be able to sorb sufficient quantities of the heavy metal containing compounds formed by the catalytic action of the vanadium incorporated ZrO₂ sorbent. These heavy metal containing compounds may then be sorbed by the lesser expensive heavy metal compound sorbent material located downstream from the vanadium incorporated ZrO₂ sorbent.

The heavy metal compound removal system preferably results in the sorption of at least about 80% by weight of the heavy metal containing compounds that break through the vanadium incorporated ZrO₂ sorbent material, more preferably at least about 90% by weight, and most preferably at least about 95% by weight.

In addition to the vanadium incorporated ZrO₂ sorbent material becoming saturated, the overall sorptive efficiency may be effected by the presence of NO_x and SO_x compounds present in the flue gas. For example, SO₂ contained in the flue gas stream may be oxidized to SO₃ and then converted to H₂SO₄ in the presence of water. The H₂SO₄ then may fill the pores of the vanadium incorporated ZrO₂ sorbent thereby decreasing the sorptive capacity thereof and blocking active catalyst sites. Therefore, it is preferable to employ an upstream NO_x and SO_x removal process in order to avoid fouling of the vanadium incorporated ZrO₂ sorbent material. Any conventional NO_x and SO_x removal process would be suitable for use with the present invention. The NO_x and SO_x removal process should preferably remove at least about 50% by weight of all NO_x and SO_x present in the flue gas stream. It is preferable for the flue gas stream immediately prior to contact with the vanadium incorporated ZrO₂ sorbent to comprise less than about 400 ppm NO_x, more preferably less than about 250 ppm, and most preferably less than about 150 ppm. Likewise, it is preferable for the flue gas stream immediately prior to contact with the vanadium incorporated ZrO₂ sorbent to comprise less than about 800 ppm SO_x, more preferably less than about 500 ppm, and most preferably less than about 400 ppm.

The heavy metal compound removal system is capable of performing

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effectively even at high flue gas flow rates (i.e., >10,000 gas hourly space velocity). The sorbent material used in the heavy metal compound removal system may be placed in a fluidized or packed bed vessel, however, as with the vanadium incorporated ZrO₂ sorbent material system above, the pressure drop of the flue gas stream should be minimized to avoid requiring the use of additional equipment to compensate for the pressure drop.

EXAMPLE

The following example illustrates preferred sorbent materials and methods of making the same in accordance with the present invention. This example should not be taken as limiting the scope of the present invention in any way.

In this example, a sorbent material according to the present invention was prepared by first dissolving 51.4 g ammonium metavanadate (NH₄VO₃) in 440 g of oxalic acid. In order to maintain the vanadium in its +5 oxidation state (indicated by a reddish color), hydrogen peroxide was added drop wise to the solution (approximately 120 drops were used). The NH₄VO₃ solution was then mixed with 200 g of ZrO₂ in four steps thereby impregnating the NH₄VO₃ onto the ZrO₂ by incipient wetness. In each step, 125 g of the NH₄VO₃ solution was added and the material dried at 248°F (120°C) for one hour before beginning the next step. Next, 20 g aliquots of the material were calcined at 45-degree increments from 572-932°F (300-500°C).

Two aliquots were tested for efficacy in removing elemental mercury entrained in an air stream at a concentration of approximately 1000 µg/m³ (ppb w/v); the first aliquot being the material calcined at 572°F (300°C) and the second aliquot being the material calcined at 842°F (450°C). Portions of the sorbent were placed in a fixed bed reactor, the temperature of which was held constant at 302°F (150°C). The air flow rate through the fixed bed reactor was set at a gas hourly space velocity of approximately 10,000. The air stream entering and exiting the fixed bed reactor was periodically analyzed using a Jerome Mercury Analyzer.

FIG. 1 shows the mercury uptake versus the mercury breakthrough of the two sorbent materials tested. For purposes of comparison, literature data for sulfur

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impregnated activated charcoal (SIAC), a conventional sorbent for this application, is also shown. The vanadium/ZrO₂ materials demonstrated excellent capacity for sequestering mercury when compared with the SIAC literature data. The material calcined at 572°F (300°C) exhibited a greater capacity over the long term versus the material calcined at 842°F (450°C). However, both materials performed much better than the activated charcoal. FIG. 2 further demonstrates the effectiveness of the sorbent materials in removing mercury from the air stream in terms of efficiency of the sorbent versus mercury uptake. The sorbent material calcined at 572°F (300°C) exhibited superior efficiency in sequestering the mercury. The efficiency of the material calcined at 842°F (450°C) initially matched that of the material calcined at 572°F (300°C). However, this efficiency dropped off after about 500 µg/g Hg uptake. In sum, the test results indicate that the calcine temperature effects the mercury sorbing capacity and efficiency of the vanadium/ZrO₂ materials. Furthermore, the vanadium/ZrO₂ sorbents tend to remain active even when heated to extreme temperatures, such as those required to remove mercury from spent sorbent material. This indicates that the sorbent is capable of being regenerated without significant loss of activity.

CLAIMS

1. A porous sorbent material comprising particles of a ZrO_2 support having incorporated onto, into, or onto and into at least one source of vanadium selected from the group consisting of vanadate ions, vanadium oxide, and combinations thereof, said material comprising at least about 5% by weight vanadium.
2. A composition in accordance with claim 1, wherein said ZrO_2 particles have an average particle size of between about 0.01-20 mm.
3. A composition in accordance with claim 1, wherein said material comprises between about 7-40% by weight vanadium.
4. A composition in accordance with claim 1, wherein said vanadium oxide compound comprises V_2O_5 , a hydrate of V_2O_5 , a peroxo complex of vanadium oxide, or mixtures thereof.
5. A composition in accordance with claim 1, wherein said ZrO_2 support material comprises at least about 50% by weight of the total weight of said composition.
6. A composition in accordance with claim 1, wherein said ZrO_2 support material has a surface area of at least about 75 m^2/g .
7. A composition in accordance with claim 1, wherein said source of vanadate ions comprises NH_4VO_3 .
8. A method for forming a sorbent material comprising:
 - (a) incorporating into, onto, or into and onto a porous ZrO_2 support a mixture including a source of vanadate ions, and a solvent capable of solubilizing said source of vanadate ions;
 - (b) drying said vanadate incorporated ZrO_2 material; and
 - (c) calcining said dried vanadium incorporated ZrO_2 material.
9. A method in accordance with claim 8, wherein said source of vanadate ions comprises NH_4VO_3 .
10. A method in accordance with claim 8, wherein step (a) includes

impregnating said ZrO_2 support with said source of vanadate ions.

11. A method in accordance with claim 8, wherein step (a) includes dissolving said source of vanadate ions in said solvent followed by the addition of said oxidizing agent so as to maintain the vanadium present in said vanadate ions in a +5 oxidation state.
12. A method in accordance with claim 8, wherein said solvent is selected from the group consisting of oxalic acid, HNO_3 , HCl , and mixtures thereof.
13. A method in accordance with claim 8, wherein said mixture further includes an oxidizing agent.
14. A method in accordance with claim 13, wherein said oxidizing agent is different from said solvent and selected from the group consisting of H_2SO_4 , HNO_3 , permanganate, ozone, H_2O_2 , and mixtures thereof.
15. A method in accordance with claim 13, wherein said oxidizing agent is present in the vanadate ion containing mixture of step (a) at a level of about 0.01-25% by weight.
16. A method in accordance with claim 8, wherein step (c) includes heating said dried vanadium incorporated ZrO_2 material to a temperature of between about 200 - 600°C (about 392-1112°F).
17. A method in accordance with claim 16, wherein step (c) includes heating said dried vanadium incorporated ZrO_2 material to a temperature of between about 250 - 450°C (about 482-842°F).
18. A method in accordance with claim 8, wherein said calcined vanadium incorporated ZrO_2 material comprises V_2O_5 , a hydrate of V_2O_5 , a peroxo complex of vanadium oxide, or mixtures thereof.
19. A method in accordance with claim 8, wherein said calcined vanadium incorporated ZrO_2 material comprises at least about 5% by weight vanadium on an elemental basis.

20. A method for forming a sorbent material comprising:
- (a) preparing a mixture comprising a source of vanadate ions and a solvent capable of solubilizing said source of vanadate ions;
 - (b) adding a quantity of an oxidizing agent to said mixture;
 - 5 (c) intimately mixing said mixture with a quantity of ZrO_2 particles;
 - (d) drying said intimate mixture thereby forming a vanadium incorporated ZrO_2 material; and
 - (e) calcining said vanadium incorporated ZrO_2 material.
21. A method in accordance with claim 20, wherein said solvent is selected
10 from the group consisting of oxalic acid, HNO_3 , HCl , and mixtures thereof.
22. A method in accordance with claim 20, wherein said oxidizing agent is different from said solvent and selected from the group consisting of H_2SO_4 , HNO_3 , permanganate, ozone, H_2O_2 , and mixtures thereof.
23. A method in accordance with claim 20, wherein said source of vanadate
15 ions comprises NH_4VO_3 .
24. A method in accordance with claim 20, wherein said oxidizing agent is added to said mixture in step (b) so as to provide from about 0.01-25% of the total weight of the mixture.
25. A method in accordance with claim 20, wherein step (c) includes
20 impregnating said ZrO_2 particles with said vanadate ions.
26. A method in accordance with claim 20, wherein step (d) includes heating said mixture to a temperature of at least about $100^\circ C$ (about $212^\circ F$).
27. A method in accordance with claim 20, wherein step (b) includes the drop wise addition of said oxidizing agent to said mixture.
- 25 28. A method in accordance with claim 20, wherein said oxidizing agent is added in a sufficient quantity so as to maintain the vanadium present in said vanadate ions in a +5 oxidation state.

29. A method in accordance with claim 20, wherein step (e) includes heating said vanadium incorporated ZrO_2 material to a temperature of between about 200 - 600°C (about 392-1112°F).
30. A method in accordance with claim 29, wherein step (e) includes heating
5 said vanadium incorporated ZrO_2 material to a temperature of between about 250 - 450°C (about 482-842°F).
31. A method in accordance with claim 20, wherein said vanadium incorporated ZrO_2 material comprises V_2O_5 , a hydrate of V_2O_5 , a peroxy complex of vanadium oxide, or mixtures thereof.
- 10 32. A method in accordance with claim 20 wherein said vanadium incorporated ZrO_2 material comprises at least about 5% by weight vanadium on an elemental basis.
33. A method of removing at least one heavy metal or heavy metal containing compound from a fluid stream, said method comprising the step of:
- 15 (a) contacting said fluid stream with a porous ZrO_2 support material having incorporated onto, into, or onto and into a vanadium containing compound for sorption of at least a portion of said at least one heavy metal or heavy metal containing compound.
34. A method in accordance with claim 33, wherein said vanadium
20 incorporated support material oxidizes said heavy metal into an oxidized heavy metal species or heavy metal containing compound.
35. A method in accordance with claim 33, wherein said vanadium compound comprises V_2O_5 , a hydrate of V_2O_5 , a peroxy complex of vanadium oxide, or mixtures thereof.
- 25 36. A method in accordance with claim 33, wherein said contacting step results in a pressure drop in said fluid stream of less than about 138 kPa (about 20 psia).
37. A method in accordance with claim 36, wherein said contacting step results in a pressure drop in said fluid stream of less than about 69 kPa (about 10 psia).

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38. A method in accordance with claim 33, wherein said fluid stream has a temperature between about 10 - 204°C (about 50-400°F) during said contacting step.

39. A method in accordance with claim 33, wherein said fluid stream comprises at least one heavy metal or compound containing a heavy metal selected from the group consisting of arsenic, beryllium, lead, cadmium, chromium, nickel, zinc, mercury, and barium.

40. A method in accordance with claim 39, wherein said at least one heavy metal is mercury.

41. A method in accordance with claim 33, wherein said vanadium incorporated support material comprises finely divided particles that are suspended in said fluid stream during said contacting step, pelletized particles placed in a fixed or fluidized bed, monoliths, or combinations thereof.

42. A method in accordance with claim 33, wherein said contacting step results in the sorption of at least about 80% by weight of the at least one heavy metal or heavy metal containing compound contained in said fluid stream.

43. A method in accordance with claim 33, wherein said vanadium incorporated support material is capable of sorbing at least about 1 atom of said heavy metal per every 5 atoms of vanadium.

44. A method in accordance with claim 33, wherein said vanadium incorporated material comprises at least about 5% by weight vanadium on an elemental basis.

45. A process for the removal of at least one heavy metal or heavy metal containing compound from a flue gas stream produced by the combustion of a hydrocarbon-containing fuel comprising the steps of:

(a) contacting said flue gas stream with a first sorbent material comprising a porous ZrO_2 support material having incorporated onto, into, or onto and into a vanadium containing compound for sorbing at least a portion of said at least one heavy metal or heavy

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metal containing compound present in said flue gas stream; and
(b) contacting said flue gas with a second sorbent material different
from said first sorbent material for sorbing at least a portion of
said at least one heavy metal-containing compound not sorbed
during step (a).

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46. A process as recited in claim 45, wherein said vanadium incorporated support material oxidizes said heavy metal into an oxidized heavy metal species or heavy metal containing compound during step (a).

47. A process as recited in claim 45, wherein said second sorbent material comprises a material selected from the group consisting of porous zeolite materials, amorphous carbons, and combinations thereof.

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48. A process as recited in claim 47, wherein said amorphous carbons are selected from the group consisting of activated charcoal, activated carbon, and combinations thereof.

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49. A process as recited in claim 47, wherein said porous zeolite material comprises ZSM-5 zeolite.

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50. A process as recited in claim 45, wherein said flue gas stream comprises at least one heavy metal or compound containing a heavy metal selected from the group consisting of arsenic, beryllium, lead, cadmium, chromium, nickel, zinc, mercury, and barium.

51. A process as recited in claim 50, wherein said at least one heavy metal is mercury.

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52. A process as recited in claim 45, wherein said vanadium compound comprises V_2O_5 , a hydrate of V_2O_5 , a peroxy complex of vanadium oxide, or mixtures thereof.

53. A process as recited in claim 45, wherein step (a) results in a pressure drop in said flue gas stream of less than about 138 kPa (about 20 psia).

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54. A process as recited in claim 45, wherein said flue gas stream has a temperature between about 10 - 204°C (about 50-400°F) during step (a).
55. A process as recited in claim 45, wherein said vanadium incorporated support material comprises finely divided particles that are suspended in said flue gas stream during step (a), pelletized particles placed in a fixed or fluidized bed, monoliths, or combinations thereof.
56. A process as recited in claim 45, wherein step (a) results in the sorption of at least about 80% by weight of said at least one heavy metal or heavy metal containing compound contained in said flue gas stream.
57. A process as recited in claim 45, wherein step (b) results in the removal of at least about 80% by weight of said at least one heavy metal compound from said flue gas stream.
58. A process as recited in claim 45, wherein said vanadium incorporated material comprises at least about 5% by weight vanadium on an elemental basis.
59. A process as recited in claim 45, wherein prior to step (a) said process includes removal of at least about 50% by weight of all NO_x and SO_x present in said flue gas.
60. A process as recited in claim 45, wherein said flue gas stream comprises less than about 400 ppm NO_x and less than about 800 ppm SO_x immediately prior to step (a).

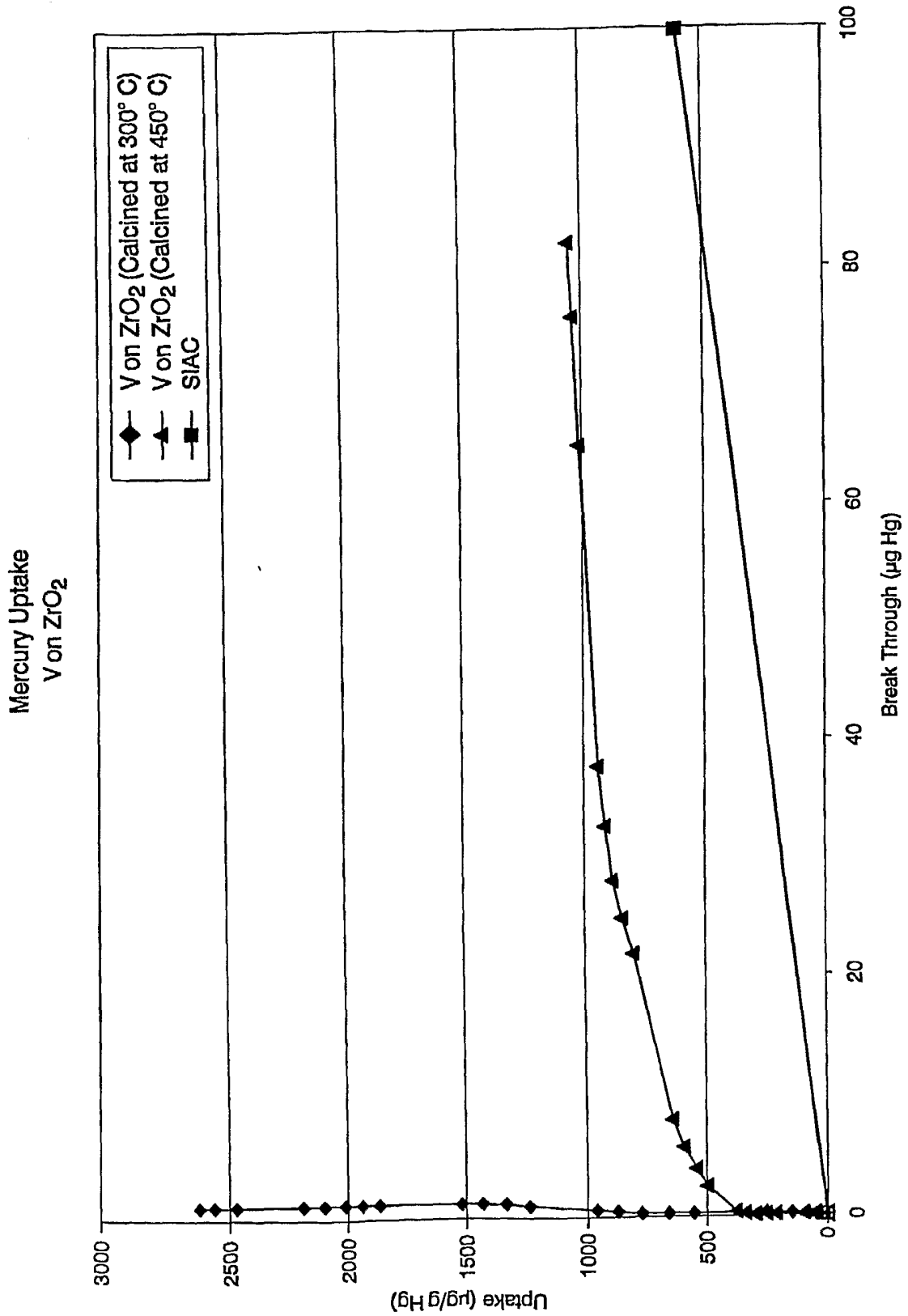


FIG. 1

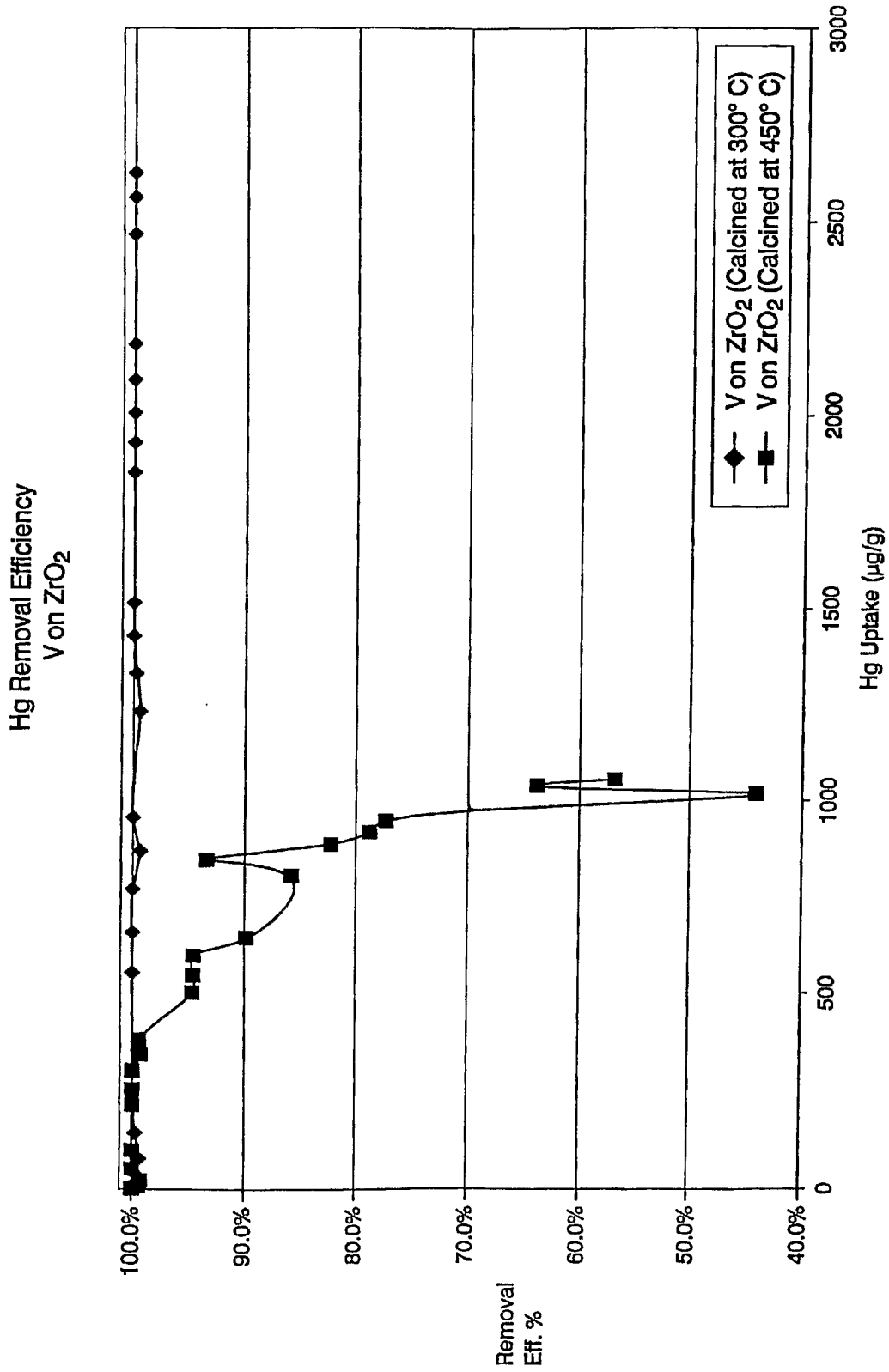


FIG. 2