



(86) Date de dépôt PCT/PCT Filing Date: 2005/08/19
(87) Date publication PCT/PCT Publication Date: 2006/03/16
(85) Entrée phase nationale/National Entry: 2007/02/26
(86) N° demande PCT/PCT Application No.: US 2005/029715
(87) N° publication PCT/PCT Publication No.: 2006/028686
(30) Priorités/Priorities: 2004/09/01 (US10/932,177);
2005/08/18 (US11/207,154)

(51) Cl.Int./Int.Cl. *B01J 20/34* (2006.01),
B01D 53/00 (2006.01), *C10G 25/05* (2006.01),
C10K 1/32 (2006.01)

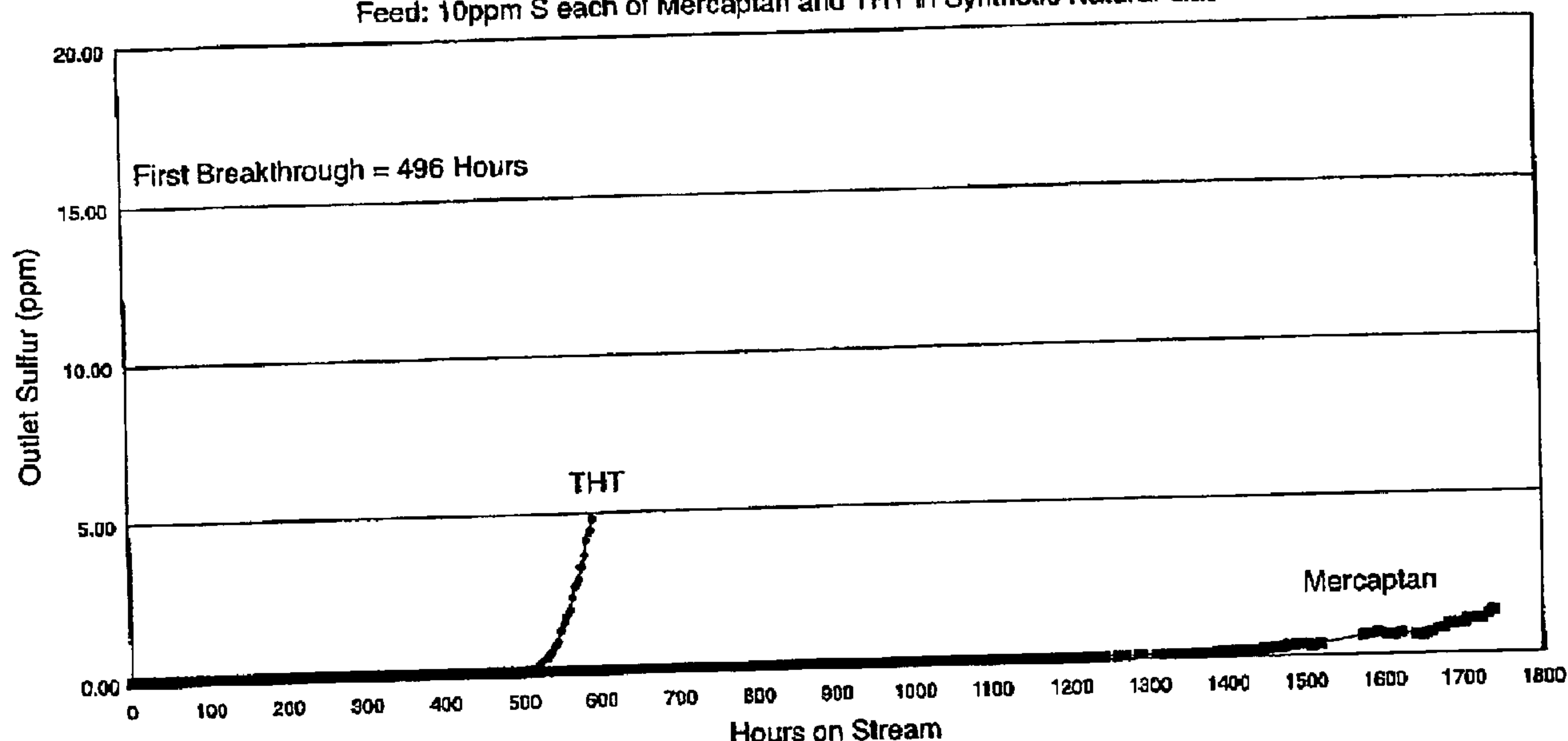
(71) Demandeurs/Applicants:
SUD-CHEMIE INC., US;
ZEOCHEM LLC, US

(72) Inventeurs/Inventors:
WESTON, ERIC J., US;
SPIVEY, R. STEVE, US;
WESTON, KERRY C., US

(74) Agent: SMART & BIGGAR

(54) Titre : SYSTEME DE DESULFURATION ET PROCEDE POUR DESULFURER UN FLUX DE COMBUSTIBLE
(54) Title: A DESULFURIZATION SYSTEM AND METHOD FOR DESULFURIZING A FUEL STREAM

Zeolite (A) and Selective Chemical Sorbent (A) - 75/25 Ratio
Test Condition (A)
Feed: 10ppm S each of Mercaptan and THT in Synthetic Natural Gas



(57) Abrégé/Abstract:

A method for producing a substantially desulfurized hydrocarbon fuel stream at temperatures less than 100°C including providing a nondesulfurized fuel cell hydrocarbon fuel stream and passing the fuel stream through a sequential sulfur adsorbent bed system containing at least one selective sulfur adsorbent and a calcium exchanged zeolite to produce a substantially desulfurized hydrocarbon fuel stream.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
16 March 2006 (16.03.2006)

PCT

(10) International Publication Number
WO 2006/028686 A1

(51) International Patent Classification:

B01J 20/34 (2006.01) **B01D 53/00** (2006.01)
C10G 25/05 (2006.01) **C10K 1/32** (2006.01)

(21) International Application Number:

PCT/US2005/029715

(22) International Filing Date: 19 August 2005 (19.08.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

10/932,177 1 September 2004 (01.09.2004) US
11/207,154 18 August 2005 (18.08.2005) US

(71) Applicants (for all designated States except US): **SUD-CHEMIE INC.** [US/US]; 1600 W. Hill Street, Louisville, KY 40210 (US). **ZEOCHEM, LLC** [US/US]; 1600 W. Hill Street, Louisville, KY 40210 (US).

(72) Inventors: **WESTON, Eric, J.**; 329 Minnie Lane, Shepherdsville, KY 40165 (US). **SPIVEY, Steve, R.**; 4109 Stony Ridge Road, #47, Louisville, KY 40299 (US). **WESTON, Kerry, C.**; 6301 Lure Court, Louisville, KY 40229 (US).

(74) Agent: **COX, Scott, R.**; Lynch, Cox, Gilman & Mahan, P.S.C., 500 W. Jefferson St., Suite 2100, Louisville, KY 40202 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

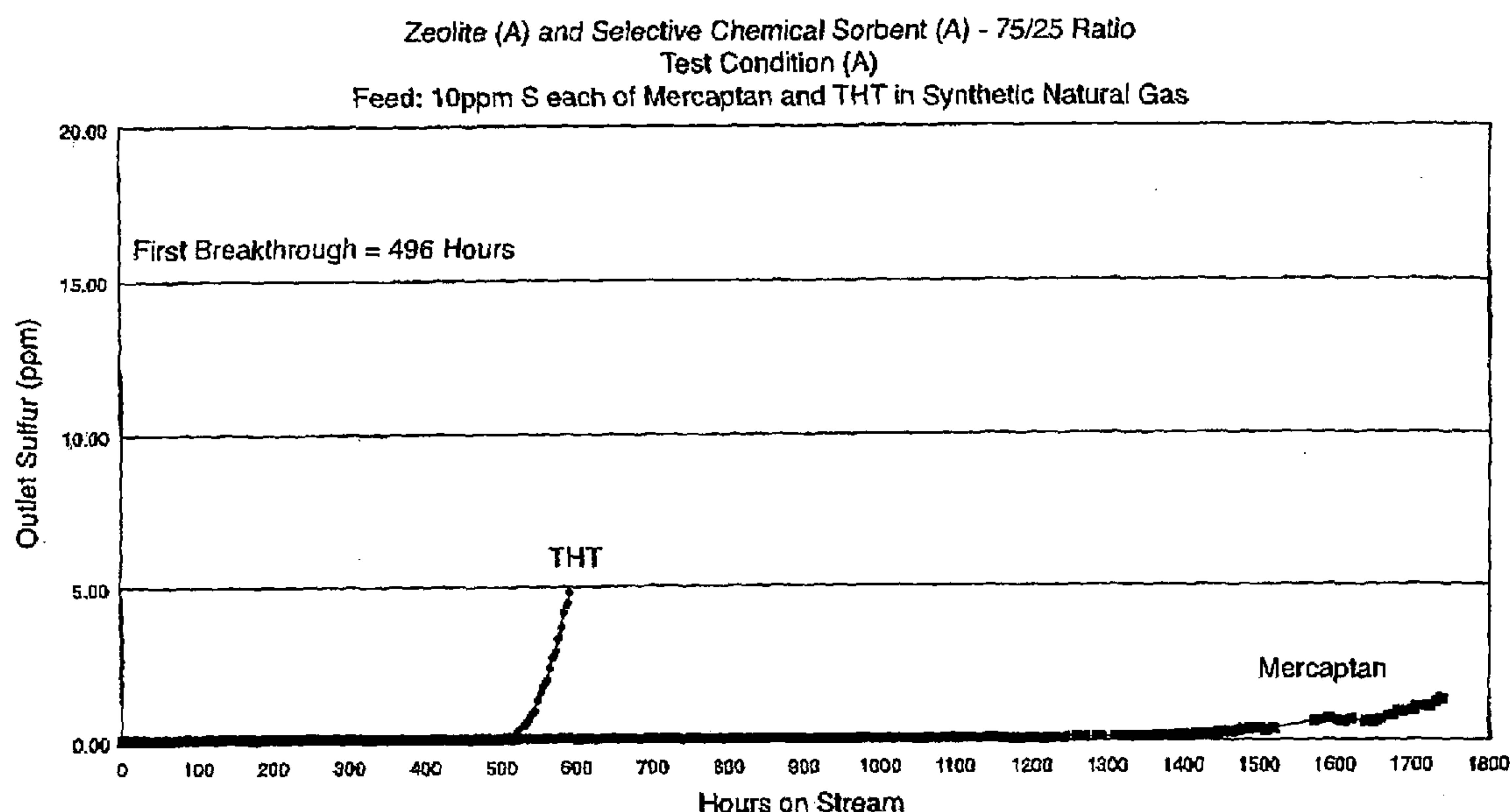
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE,

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(54) Title: A DESULFURIZATION SYSTEM AND METHOD FOR DESULFURIZING A FUEL STREAM



(57) Abstract: A method for producing a substantially desulfurized hydrocarbon fuel stream at temperatures less than 100°C including providing a nondesulfurized fuel cell hydrocarbon fuel stream and passing the fuel stream through a sequential sulfur adsorbent bed system containing at least one selective sulfur adsorbent and a calcium exchanged zeolite to produce a substantially desulfurized hydrocarbon fuel stream.

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WO 2006/028686 A1



LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE,

LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

5 **TITLE**

A DESULFURIZATION SYSTEM AND METHOD FOR DESULFURIZING A FUEL STREAM

BACKGROUND OF INVENTION

10 The present invention relates to a novel method for producing a substantially desulfurized hydrocarbon fuel stream, particularly for hydrogen generation, and more particularly utilized within a fuel cell processing train, by passing a nondesulfurized hydrocarbon fuel stream,
15 particularly natural gas, propane or liquefied petroleum gas (LPG), through a sequential sulfur adsorbent bed system at temperatures less than 100°C, wherein the sequential sulfur adsorbent bed system contains a zeolite sulfur adsorbent and at least one selective sulfur adsorbent. The present
20 invention further relates to a system for generating electricity within a fuel cell processing train from a substantially desulfurized hydrocarbon fuel stream, particularly desulfurized natural gas, propane or LPG, wherein the hydrocarbon fuel stream is desulfurized using
25 the above-described sequential sulfur adsorbent bed system. The present invention further includes a desulfurization system used for hydrogen generation, particularly within a fuel cell processing train for desulfurizing hydrocarbon fuel streams, particularly natural gas, propane or LPG, at

5 temperatures as low as ambient temperatures.

For hydrogen generation, particularly for use in a conventional low temperature fuel cell processing train, such as a proton exchange membrane (PEM) fuel cell, which is suitable for use in a stationary application or in a
10 vehicle, such as an automobile, the hydrocarbon fuel stream can be derived from a number of conventional fuel sources with the preferred fuel sources including natural gas, propane and LPG. In a conventional hydrogen generation system, particularly a fuel cell processing train, the
15 hydrocarbon fuel stream is passed over and/or through a desulfurization system to be desulfurized. The desulfurized hydrocarbon fuel stream for such fuel cell processing train then flows into a reformer wherein the fuel stream is converted into a hydrogen-rich fuel stream. From the
20 reformer the fuel stream passes through one or more heat exchangers to a shift converter where the amount of CO in the fuel stream is reduced. From the shift converter the fuel stream again passes through various heat exchangers and then through a selective oxidizer or selective methanizer
25 having one or more catalyst beds, after which the hydrogen rich fuel stream flows to the fuel cell stack where it is utilized to generate electricity.

Raw fuels, in gaseous or liquid phase, particularly

5 natural gas, propane and LPG, are useful as a fuel source
for hydrogen generation, particularly for fuel cell
processing trains. Unfortunately, virtually all raw fuels
contain relatively high levels, up to as high as 1,000 ppm
or so, but typically in the range of 20 to 500 ppm, of
10 various naturally occurring sulfur compounds, such as, but
not limited to, carbonyl sulfide, hydrogen sulfide,
thiophenes, such as tetra hydro thiophene, dimethyl sulfide,
various mercaptans, disulfides, sulfoxides, other organic
sulfides, higher molecular weight organic sulfur compounds,
15 and combinations thereof. In addition, because hydrocarbon
fuel streams, particularly natural gas, propane and LPG, may
have different sources of origin, the quantity and
composition of the sulfur compounds that may be present in
the fuel streams can vary substantially.

20 The presence of these sulfur-containing compounds in a
hydrocarbon fuel stream can be very damaging to components
of the fuel cell processing train, including the fuel cell
stack itself, and must therefore be substantially removed.
If not substantially removed, the sulfur compounds shorten
25 the life expectancy of components of the fuel cell
processing train.

An especially efficient desulfurization system is
necessary for use in such fuel cell processing trains as

5 they generally only contain a single desulfurization system.
Further, desulfurization systems for such uses must have
high capacity, as they may need to be in use for an extended
period of time before replacement.

Several processes, conventionally termed
10 "desulfurization," have been employed for the removal of
sulfur from gas and liquid fuel streams for hydrogen
generation. Adsorption of sulfur-contaminated compounds from
these hydrocarbon streams using a "physical" sulfur
adsorbent is the most common method for removal of sulfur
15 compounds from such hydrocarbon fuel streams because of
their relatively low capital and operational costs. (For
purposes of this specification, the terms "adsorption" and
"absorption" have the same, all inclusive meaning.) While
physical adsorbents are useful, they can be subject to
20 desorption of the sulfur compounds from the adsorbent under
certain operating conditions. In addition, there are often
limits on the quantity of sulfur compounds which can be
adsorbed by such physical sulfur adsorbents.

An additional type of adsorbent that has been useful as
25 a desulfurization agent is a "chemical" sulfur adsorbent.
However, chemical desulfurization normally requires the
desulfurization bed to be heated to temperatures of about

5 150°C to 400°C before the nondesulfurized hydrocarbon fuel streams can be passed through the chemical adsorbent desulfurization system. In addition, other operational problems may occur when chemical desulfurization processes are utilized.

10 While many different desulfurization processes have been suggested for hydrocarbon fuel streams, there is still a need for improved processes for desulfurization to achieve enhanced adsorption of sulfur components over an extended range of sulfur concentrations, especially at relatively low
15 operating temperatures and pressures, for extended periods of time. Further, there is a need for the desulfurization system to adsorb substantial quantities of a wide range of sulfur compounds, including particularly hydrogen sulfide, carbonyl sulfide, tetra hydro thiophene, dimethyl sulfide,
20 various mercaptans, disulfides, sulfoxides, other organic sulfides, various higher molecular weight sulfur-containing compounds and combinations thereof. Further, it is important that the desulfurization system absorb this broad range of sulfur compounds effectively for an extended period
25 of time to delay "breakthrough" of sulfur compounds as long as possible. "Breakthrough" occurs when the level of any sulfur compound remaining in the feed stream after

5 desulfurization is above a predetermined level. Typical
"breakthrough" levels for sulfur compounds occur at 1 ppm or
so. In addition, breakthrough by virtually any one of the
sulfur compounds present in the hydrocarbon fuel stream is
disadvantageous as substantially all sulfur compounds cause
10 damage to components of a hydrogen generation system,
particularly for a fuel cell processing train.

In addition, some prior art adsorbents, while effective
as adsorbents for some sulfur compounds, can synthesize the
production of additional sulfur compounds even as they are
15 removing some of the sulfur compounds that are present in
the hydrocarbon fuel stream. (These additional sulfur
compounds are referred to herein as "synthesized sulfur
compounds.") It is important that the desulfurization
system avoid the production of these synthesized sulfur
20 compounds to the greatest extent possible and for the
longest period of time possible.

These and further aspects of the invention will be
apparent from the foregoing description of preferred
embodiments of the invention.

25

SUMMARY OF INVENTION

The present invention is a process for supplying a
substantially desulfurized hydrocarbon fuel stream for

5 hydrogen generation, particularly for use in a fuel cell
processing train comprising providing a nondesulfurized
hydrocarbon fuel stream, preparing a desulfurization system
comprising a sequential sulfur adsorbent bed system
comprising a calcium exchanged zeolite sulfur adsorbent and
10 at least one selective sulfur adsorbent, and passing the
nondesulfurized hydrocarbon fuel stream through or over the
desulfurization system at a temperature optimally less than
100°C to produce a substantially desulfurized hydrocarbon
fuel stream with desulfurization levels as low as about 50
15 ppb or so. The composition and choice of the selective
sulfur adsorbent(s) and the sequence of use of the selective
sulfur adsorbent(s) and the calcium exchanged zeolite within
the desulfurization system depends on the composition of the
sulfur compounds which are present in that fuel stream.

20 The invention is also a system for generating
electricity from a fuel cell processing train by use of a
substantially desulfurized hydrocarbon fuel stream
comprising preparing a fuel cell processing train containing
the desulfurization system described above, passing a
25 nondesulfurized hydrocarbon fuel cell fuel stream through
the desulfurization system at a temperature preferably less
than 100°C, and introducing the substantially desulfurized

5 hydrocarbon fuel stream to the remaining components of the fuel cell processing train.

The invention is also a desulfurization system for hydrogen generation, particularly for use in a fuel cell processing train, comprising an inlet for receiving a
10 nondesulfurized hydrocarbon fuel stream, particularly natural gas, propane or LPG, the sequential adsorbent bed system described above, and an outlet for passing a substantially desulfurized hydrocarbon fuel stream downstream to the remaining components of the hydrogen
15 generation system.

The invention is also a sequential sulfur adsorbent bed system for hydrogen generation, particularly for use in a fuel cell processing train comprising selective sulfur adsorbent(s) and a calcium exchanged zeolite. The choice of
20 the particular selective sulfur adsorbent or absorbents and the sequence of use of the selective sulfur adsorbent or absorbents and the zeolite within the sequential sulfur adsorbent bed depends upon the composition and quantity of the sulfur compounds that are present in the hydrocarbon
25 fuel stream. One or more selective sulfur adsorbents can be utilized with the calcium exchanged zeolite to form the sequential adsorbent bed system of the invention. One particularly preferred selective sulfur adsorbent comprises

5 one or more manganese compounds, iron oxide and a high surface area carrier, particularly alumina. An alternative preferred selective sulfur adsorbent comprises one or more manganese compounds, copper oxide and a binder material.

Brief Description of Drawings

10 Figure 1 is a graph showing the performance of the calcium exchanged zeolite discussed in Example 1 for the removal of certain sulfur compounds from a synthetic natural gas feed stream.

Figure 2 is a graph showing the performance of the
15 selective sulfur adsorbent of Example 2 for the removal of the sulfur compounds of Example 1 from the synthetic natural gas feed stream of Example 1.

Figure 3 is a graph showing the performance, as discussed in Example 3, of a combination of the zeolite of
20 Example 1 with the selective sulfur adsorbent of Example 2 for the removal of the sulfur compounds of Example 1 from the synthetic natural gas feed stream of Example 1.

Disclosure of a Preferred Embodiment of the Invention

25 The invention includes a method for supplying a substantially desulfurized hydrocarbon fuel stream to a hydrogen generation system, particularly a fuel cell processing train. Raw fuel for use in such a hydrogen

5 generation system, particularly a fuel cell processing
train, such as natural gas, propane and LPG, must be
desulfurized prior to use because of the presence of
relatively high levels of naturally occurring sulfur
compounds, such as, but not limited to, hydrogen sulfide,
10 carbonyl sulfide, thiophenes, such as tetra hydro thiophene,
dimethyl sulfide, mercaptans (including ethyl, methyl,
propyl and tertiary butyl mercaptan), other sulfides,
various higher molecular weight organic sulfur compounds and
combinations thereof. These sulfur compounds can damage
15 components of the hydrogen generation system and the fuel
cell processing train. While numerous combinations and
quantities of these sulfur compounds may be present in the
fuel stream, in some situations, the sulfur compounds
present in the fuel stream may be limited to only one or two
20 such sulfur compounds. Where the raw fuel stream comprises
natural gas, which is in a gaseous state at operating
temperatures below 100°C, the level of sulfur compounds, such
as carbonyl sulfide, hydrogen sulfide, tetra hydro
thiophene, dimethyl sulfide, mercaptans, other organic
25 sulfur compounds, and combinations thereof may be as high as
about 100 ppm. The presence of such high levels of sulfur
compounds, if not removed, results in the poisoning of

5 components of the fuel cell processing train and may foul the fuel cell stack itself. Substantially complete removal of all of the sulfur compounds is necessary as the presence of even modest quantities of even a single sulfur compound can damage the components of the fuel cell processing train.

10 While the desulfurization system of the invention can be utilized for a number of different hydrogen generation processes, one particularly preferred utilization is within a fuel cell processing train. For purposes of this specification all hydrogen generation systems are included,
15 although one preferred use is within a fuel cell processing train.

The inventors have surprisingly discovered that substantial desulfurization of a hydrocarbon fuel stream for fuel cell processing trains down to levels as low as 50 ppb
20 or so can be achieved when a sequential sulfur adsorbent bed system is used as the desulfurization system comprising one or more selective sulfur adsorbents used in combination with a zeolite adsorbent, particularly a calcium exchanged zeolite, more particularly a calcium exchanged X zeolite.
25 The composition and sequence of use of the components of the sequential sulfur adsorbent bed system can be adjusted depending on the composition and quantity of the sulfur compounds that are present in the hydrocarbon feed stream.

5 The selective sulfur adsorbent(s) of the invention is selected from a wide variety of adsorbents. As used within this application a "selective sulfur adsorbent" is a material that preferentially absorbs at least one of the sulfur compounds that are commonly present in hydrocarbon
10 fuel cell fuel streams, particularly natural gas, propane or LPG, such as hydrogen sulfide, carbonyl sulfide, tetra hydro thiophene, dimethyl sulfide, mercaptans, particularly ethyl, methyl, propyl, and tertiary butyl mercaptans and combinations thereof, at a temperature below 100°C and
15 pressures of about 10-250 psig or so.

Each selective sulfur adsorbent selectively adsorbs one or more of the sulfur compounds that are commonly present in the hydrocarbon fuel cell fuel stream, preferably natural gas. However, each of these adsorbents may be less or more
20 effective than other of the selective sulfur adsorbents for the adsorption of particular sulfur compounds or combinations of these compounds. Further, additional problems can be created in the feed stream when some of the selective sulfur adsorbents are used alone as the sulfur
25 adsorbent, as these selective sulfur adsorbents can synthesize existing sulfur compounds into different, higher molecular weight synthesized sulfur compounds that are not removed from the fuel stream by the particular selective

5 sulfur adsorbent.

It has been surprisingly discovered that the desulfurization system can be substantially enhanced by utilizing a zeolite adsorbent particularly a calcium exchanged zeolite, and more particularly a calcium exchanged
10 X zeolite, in combination with the selective sulfur adsorbent. Further, adsorption of a broader range of sulfur compounds from the hydrocarbon fuel cell fuel streams may occur when more than one selective sulfur adsorbent is used in combination with the zeolite adsorbent in the sequential
15 sulfur adsorbent bed system. In particular, the combination of one or more selective sulfur adsorbents with the calcium exchanged zeolite adsorbent performs surprisingly better than the individual selective sulfur adsorbents or the calcium exchanged zeolite when used individually. In
20 addition, the choice and arrangement of the selective sulfur adsorbent(s) and the zeolite within the sequential sulfur adsorbent bed system can reduce the likelihood of the production of synthesized sulfur compounds that are sometimes created when only a single selective sulfur
25 adsorbent is utilized in the desulfurization system.

It has been further discovered that the removal of various combinations of sulfur compounds can be enhanced by the specific arrangement of the adsorbents in the sequential

5 sulfur adsorbent bed system. For example, for the removal
of one type or group of sulfur compounds, it is preferable
to place the calcium exchanged zeolite in the sequential
sulfur adsorbent bed prior to the selective sulfur adsorbent
while for other sulfur compounds or combinations of sulfur
10 compounds, it is preferable for the non-desulfurized
hydrocarbon fuel cell fuel stream to contact one of the
selective sulfur adsorbents prior to contacting the calcium
exchanged zeolite. For other non-desulfurized hydrocarbon
fuel cell fuel streams, it may be preferable to use two or
15 more selective sulfur adsorbents, wherein one or more of
these selective sulfur adsorbents are placed before or after
the zeolite adsorbent in the sequential sulfur adsorbent bed
system.

Sulfur adsorption by this system is further enhanced
20 because some sulfur compounds, which may be synthesized to
larger and more difficult to remove sulfur compounds by a
particular selective sulfur adsorbent, are removed from the
feed stream by the zeolite adsorbent, particularly the
calcium-exchanged zeolite adsorbent, prior to synthesis by
25 the selective sulfur adsorbent.

Suitable selective sulfur adsorbents are selected from
a group of adsorbents including, but not limited to, a group
of manganese-based adsorbents, such as an adsorbent

5 comprising substantially manganese compounds, an adsorbent
which includes manganese compounds, copper oxide and a
binder and an adsorbent which includes manganese compounds,
iron oxide and a high surface area carrier, particularly
alumina. Other useful selective sulfur adsorbents for this
10 desulfurization system may include, but are not limited to,
zinc oxide with or without a carrier, such as alumina;
activated carbon with copper oxide; a zinc oxide/copper
oxide blend preferably containing small quantities of carbon
and alumina; copper oxide with alumina; and a copper
15 oxide/zinc oxide blend mixed with alumina. Other useful
selective sulfur adsorbents may include nickel on silica or
alumina and other known selective sulfur adsorbents
containing copper, zinc, molybdenum and cobalt compounds.
Various quantities of the individual components of each of
20 these selective sulfur adsorbents can be utilized and the
quantity of the individual components can be modified to
enhance the adsorption capacity of the overall
desulfurization system, depending on the particular sulfur
compounds that are present in the hydrocarbon fuel cell fuel
25 stream and the quantity thereof.

In one particularly preferred embodiment, the selective
sulfur adsorbent contains one or more manganese compounds
blended with iron oxide on a high surface area support,

5 preferably a high surface area support comprising alumina, silica, silica-alumina, titania, and other inorganic refractory oxides, with a more preferred support being a high surface area alumina. By "high surface area" the inventors are describing a support with a surface area
10 greater than 100 m²/g.

The inventors have surprisingly discovered that the ability of the manganese compound(s)/iron oxide selective sulfur adsorbent to adsorb sulfur compounds is enhanced when the high surface area support is a high surface area
15 alumina. Adsorbents comprising manganese compound(s)/iron oxide materials with high surface area alumina perform better and adsorb higher levels of sulfur compounds than when the carrier comprises other inorganic materials, even with similar surface areas. Any type of alumina with a
20 surface area above 100 m²/g is within the scope of the invention. The preferred carrier comprises from 5 to 25% by weight, preferably from 5 to 20% by weight, and most preferably from 5 to 15% by weight of the total weight of this selective sulfur adsorbent. The primary function of
25 the support material is to provide a large and accessible surface area for deposition of the active metal compounds.

The metal compounds which are deposited on or with the high surface area support of this selective sulfur

5 adsorbent, other than the one or more manganese compound(s),
include iron oxide. In a preferred embodiment the iron
oxide and manganese compound(s) together comprise at least
60% by weight, preferably at least 70% by weight and most
preferably at least 80% to 90% of this selective sulfur
10 adsorbent, by weight.

In a preferred embodiment the quantity of iron oxide
present in this selective sulfur adsorbent exceeds the
quantity of the manganese compound(s). It is preferred that
the ratio of the iron oxide to the manganese compound(s) by
15 weight, should be at least 1:1 and preferably from 1:1 to
6:1. The preferred loading of iron oxide on the support is
in the range of 40 weight percent to 80 weight percent and,
more preferably from 50 to 70 weight percent of the total
weight of the selective sulfur adsorbent. Various forms of
20 iron oxide may be used, such as FeO and Fe_2O_3 and mixtures
thereof.

The one or more manganese compound(s) comprise from 15
weight percent to 40 weight percent, preferably from 20
weight percent to 40 weight percent of the total weight of
25 the selective sulfur adsorbent. Various forms of manganese
compounds can be used including MnO_2 , Mn_2O_3 , Mn_3O_4 and $\text{Mn}(\text{OH})_4$
and mixtures thereof.

A promoter or promoters may also be added to this

5 selective sulfur adsorbent, preferably an alkali or alkaline
earth metal oxide and more preferably calcium oxide, in
quantities from 5 to 15% by weight. While calcium oxide is
the preferred promoter, other alkali or alkaline earth metal
oxides, such as magnesium oxide, may also, or alternatively,
10 be utilized with the calcium oxide.

The iron oxide/manganese compound(s) selective sulfur
adsorbent according to the present invention may be prepared
by coprecipitation, decomposition, impregnation or
mechanical mixing. Preferably, this selective sulfur
15 adsorbent is produced by coprecipitation or decomposition.
The method chosen should guarantee that there has been an
intensive blending of the components of the selective sulfur
adsorbent.

The specific pore volume of the iron oxide/manganese
20 compound(s) adsorbent produced by those procedures
determined by mercury porosimetry is preferably from 0.3
cc/g to 0.6 cc/g. In addition, this selective sulfur
adsorbent preferably has a compacted bulk density of 0.4 to
1.1 g/cc. Once the material is in its preliminary product
25 form, it can be further processed to form the final
selective sulfur adsorbent by pelletizing or extrusion.
This selective sulfur adsorbent preferably is formed into
moldings, especially in the form of spheres or pellets,

5 preferably ranging in size from 0.1 cm to 1 cm in diameter.
The surface area of this selective sulfur adsorbent is at
least 100 m²/g and preferably from 100 m²/g to 300 m²/g.

The ratio of this iron oxide/manganese compound(s) with
alumina selective sulfur adsorbent to the calcium exchanged
10 zeolite adsorbent is from 1:4 to 4:1, preferably 1:3 to 3:1,
by volume. The sequence of utilization of this selective
sulfur adsorbent in the sequential sulfur adsorbent bed
system with the calcium exchanged zeolite adsorbent
preferably places the calcium exchanged zeolite adsorbent
15 prior to this selective sulfur adsorbent.

This iron oxide/manganese compound(s) selective sulfur
adsorbent when used alone has shown especially good sulfur
adsorption when the sulfur compounds contained in a fuel
cell fuel stream comprise hydrogen sulfide, carbonyl sulfide
20 (COS), tertiary butyl mercaptan (TBM) and ethyl mercaptan
(EM). This selective sulfur adsorbent, when utilized with
the calcium-exchanged zeolite adsorbent, has shown enhanced
utility for adsorption of additional sulfur compounds that
are commonly present in a fuel cell fuel stream including
25 tetra hydro thiophene (THT) and dimethyl sulfide (DMS),
especially when the zeolite is placed in sequence before the
iron oxide/manganese adsorbent compound(s) in the sequential
sulfur adsorbent bed system. However, some common

5 hydrocarbon fuel streams do not contain these additional sulfur compounds. In this circumstance use of only the iron oxide\manganese compound(s) selective sulfur adsorbent without the calcium-exchanged zeolite adsorbent is an alternative preferred embodiment.

10 Other selective sulfur adsorbents can be utilized in combination with this selective sulfur adsorbent and zeolite adsorbent for the adsorption of particular sulfur compounds from a hydrogen generation system, such as a hydrocarbon fuel cell feed stream. For example, particularly useful
15 combinations contain the calcium exchanged zeolite adsorbent with this iron oxide/manganese compound(s) with high surface area alumina selective sulfur adsorbent and also include a selective sulfur adsorbent containing carbon with copper oxide or copper oxide/zinc oxide with alumina.
20 These selective sulfur adsorbents are described in more detail later in this specification. The sequence of utilization of these additional selective sulfur adsorbents with the zeolite adsorbent preferably places the zeolite adsorbent prior to the iron oxide/manganese compound(s) with
25 high surface area alumina with the carbon/copper oxide or the copper oxide/zinc oxide with alumina selective sulfur adsorbent placed first in the sequence of the sequential sulfur adsorbent bed stream.

5 In one preferred embodiment of this combination, the
zeolite adsorbent preferably comprises an amount equal to,
or greater than, the quantity of the other components in the
three component system in the sequential sulfur adsorbent
bed, with quantities of the zeolite adsorbent up to 80% of
10 the total sulfur adsorbents present in the sequential sulfur
adsorbent bed system with the iron oxide/manganese
compound(s) with alumina selective sulfur adsorbent
comprising up to 20% and the carbon/copper oxide or copper
oxide/zinc oxide with alumina selective sulfur adsorbent
15 also comprising up to 20% of the sequential sulfur adsorbent
bed system, by volume.

An additional preferred selective sulfur adsorbent that
can be utilized with the zeolite adsorbent in the sequential
sulfur adsorbent bed system is comprised of one or more
20 manganese compound(s), copper oxide and small quantities of
a binder. The manganese compound(s) of this selective
sulfur adsorbent may be utilized in any of the forms
previously described for the manganese compound of the
selective sulfur adsorbent described above. The manganese
25 compound(s) of this selective sulfur adsorbent comprise from
50 to 80% and preferably from 60 to 75% of this selective
sulfur adsorbent, by weight. The copper oxide comprises
from 15 to 40% and preferably from 15 to 30%, by weight, of

5 this selective sulfur adsorbent. The binder comprises from
5 to 20%, by weight, of this selective sulfur adsorbent. In
a preferred embodiment the binder may be selected from a
wide variety of clays including bentonite, diatomaceous
earth, attapulgite, kaolin, sepiolite, illite and mixtures
10 thereof. More preferably, the binder comprises bentonite
clay. Promoters may also be added to this selective sulfur
adsorbent to enhance its operating characteristics. This
adsorbent is prepared by conventional procedures. The
surface area of this manganese compound(s)/copper oxide with
15 binder selective sulfur adsorbent ranges from 100 to 300
m²/g, preferably from 200 to 300 m²/g.

This manganese compound(s)/copper oxide/binder
selective sulfur adsorbent when used alone has shown great
utility for the adsorption of hydrogen sulfide, carbonyl
20 sulfide, tertiary butyl mercaptan, ethyl mercaptan and
mixtures thereof. In addition, this manganese
compound(s)/copper oxide/binder selective sulfur adsorbent,
when utilized in sequence with the zeolite adsorbent in the
sequential sulfur adsorbent bed system, has shown
25 significant adsorption for sulfur compounds contained in
hydrocarbon fuel cell feed streams of the same type as those
described above where the selective sulfur adsorbent
composition comprises iron oxide, manganese compound(s) and

5 small quantities of a high surface area alumina.

The ratio of this selective sulfur adsorbent with the zeolite adsorbent for the removal of sulfur compounds from a fuel cell fuel stream, particularly natural gas, propane and LPG, is from 1:4 to 4:1 and preferably from 1:3 to 3:1, by
10 volume.

Other selective sulfur adsorbents, particularly of the same type, in the same quantities, and in the same sequence that may be utilized with the iron oxide/manganese compound(s) with small quantities of high surface area
15 alumina, may also be utilized with this selective sulfur adsorbent and the zeolite adsorbent to form a three component system to enhance the adsorption of particular sulfur compounds that are present in a fuel cell fuel stream. The choice of the particular selective sulfur
20 adsorbent or adsorbents used can be adjusted depending on the particular sulfur compounds that are present in the feed stream and their quantity.

An additional selective sulfur adsorbent that can be utilized with the zeolite adsorbent in the sequential sulfur
25 adsorbent bed system in place of, or in addition to, the above described selective sulfur adsorbents comprises zinc oxide alone or in combination with a carrier. While alumina is the preferred carrier, other carriers with similar

5 performance characteristics can be utilized. In a preferred
embodiment, the zinc oxide comprises at least 60%,
preferably from 60 to 95%, and more preferably from 70 to
90%, by weight, of the selective sulfur adsorbent with the
remaining portion preferably comprising alumina. Additives
10 may be added to this selective sulfur adsorbent to enhance
its capacity to absorb sulfur compounds or other performance
characteristics. The surface area of this selective sulfur
adsorbent ranges from 5 to 75 m²/g and preferably from 10 to
50 m²/g. This zinc oxide/alumina selective sulfur adsorbent
15 is prepared by conventional procedures.

The zinc oxide alumina selective sulfur adsorbent when
used alone as a sulfur adsorbent has shown good sulfur
adsorption when the sulfur compounds contained within the
fuel cell fuel stream comprise hydrogen sulfide and ethyl
20 mercaptan and mixtures thereof.

The inventors have discovered that enhanced adsorption
of sulfur compounds occurs when this zinc oxide with alumina
selective sulfur adsorbent is utilized in a sequential
sulfur adsorbent bed system with the zeolite adsorbent of
25 the invention. Preferably, the order of the adsorbents in
the sequential sulfur adsorbent bed system utilizes the zinc
oxide with alumina selective sulfur adsorbent after the
zeolite. In a preferred embodiment the ratio of the zinc

5 oxide with alumina selective sulfur adsorbent to the zeolite
adsorbent is from 1:4 to 4:1 and in a more preferred
embodiment, from 1:3 to 3:1, by volume. Although the
sequential sulfur absorbent bed system chosen may contain
only the zinc oxide with alumina selective sulfur adsorbent
10 with the zeolite adsorbent, depending upon the sulfur
content and composition within the fuel cell fuel stream,
additional selective sulfur adsorbents may also be utilized
as part of the sequential sulfur absorbent bed system either
prior to or after the zeolite adsorbent and this selective
15 sulfur adsorbent.

Another selective sulfur adsorbent that can be utilized
with the zeolite adsorbent of the invention in the
sequential sulfur adsorbent bed system is comprised of
activated carbon containing small quantities of copper
20 oxide. In a preferred embodiment the activated carbon
comprises from 80 to 95%, preferably 85 to 95%, by weight,
of this selective sulfur adsorbent with the remaining
portion comprising copper oxide. Additives may be added to
the composition to enhance its performance. The activated
25 carbon/copper oxide selective sulfur adsorbent is prepared
by conventional procedures. The surface area of the
composition ranges from 300 to 1000 m²/g, with the preferred
surface area being from 500 m²/g to 1000 m²/g. This

5 selective sulfur adsorbent is prepared by conventional procedures.

This activated carbon with copper oxide selective sulfur adsorbent when used alone has shown great utility for the adsorption of tetra hydro thiophene, tertiary butyl
10 mercaptan, ethyl mercaptan and mixtures thereof.

The quantity of the activated carbon/copper oxide selective sulfur adsorbent to be utilized with the zeolite adsorbent is at a ratio of 1:4 to 4:1, preferably 1:3 to about 3:1, by volume. Further, the preferred sequence of
15 utilization of the selective sulfur adsorbent and the zeolite adsorbent places the zeolite adsorbent ahead of the activated carbon/copper oxide selective sulfur adsorbent in the sequential sulfur adsorbent bed system.

This activated carbon with copper oxide selective
20 sulfur adsorbent has also shown good adsorption capability when used in combination with other selective sulfur adsorbents and the zeolite adsorbent for the adsorption of a broad range of sulfur compounds contained in a fuel cell feed stream.

25 Another useful selective sulfur adsorbent that can be utilized with the zeolite adsorbent in a sequential sulfur adsorbent bed system comprises copper oxide and zinc oxide with alumina, preferably with small quantities of carbon. In

5 a preferred embodiment the copper oxide comprises from 50 to 65% and more preferably from 50 to 60% of the selective sulfur adsorbent, by weight. The zinc oxide comprises from 20 to 35% of the selective sulfur adsorbent and the alumina comprises from 5 to 20%, preferably from 10 to 20% of the
10 selective sulfur adsorbent, by weight. The quantity of the carbon, if used, should be less than 10%, preferably from 1 to 10%, by weight. The surface area of this selective sulfur adsorbent containing copper oxide, zinc oxide, alumina, and preferably small quantities of carbon, is from
15 100 to 300 m²/g and preferably from 100 to 200 m²/g. The process for the preparation of this selective sulfur adsorbent is conventional.

This copper oxide/zinc oxide/alumina, preferably with small quantities of carbon, selective sulfur adsorbent when
20 used alone is especially useful for the adsorption of hydrogen sulfide, tertiary butyl mercaptan, ethyl mercaptan, carbonyl sulfide and mixtures thereof.

The ratio of this selective sulfur adsorbent to the zeolite adsorbent when used in the sequential sulfur
25 adsorbent bed system is from 1:4 to 4:1, preferably from 1:3 to 3:1, by volume. When the sulfur compound(s) to be removed from the fuel cell fuel stream include the sulfur compounds for which this selective sulfur adsorbent is

5 especially useful, the sequence for utilization of this selective sulfur adsorbent with the zeolite adsorbent requires the zeolite adsorbent to be placed prior to this selective sulfur adsorbent in the sequential sulfur adsorbent bed system. In addition to the utilization of the
10 copper oxide/zinc oxide/alumina and preferably with carbon selective sulfur adsorbent, other selective sulfur adsorbents may also be utilized, either prior to or after this selective sulfur adsorbent in the sequential sulfur adsorbent bed system of the invention.

15 An additional selective sulfur adsorbent that can be utilized with the zeolite adsorbent in the sequential sulfur adsorbent bed system, comprises manganese compound(s), used alone, which may be utilized in a number of forms including MnO_2 , Mn_2O_3 , Mn_3O_4 and $\text{Mn}(\text{OH})_4$ or mixtures thereof. The
20 surface area of the manganese compound(s) range from 100 to 300 m^2/g , and preferably from 200 to 300 m^2/g . Additional materials may be combined with the manganese compound(s) including calcium, silver and magnesium to promote the performance of the manganese compound(s). Conventional
25 methods are utilized for the formation of this selective sulfur adsorbent.

The manganese compound(s) selective sulfur adsorbent when used alone has shown great utility for the adsorption

5 of hydrogen sulfide, tertiary butyl mercaptan, ethyl mercaptan and mixtures thereof.

When used with the zeolite adsorbent in the sequential sulfur adsorbent bed system, the ratio of the manganese compound(s) utilized to the zeolite adsorbent is from 1:4 to 10 4:1 and preferably from 1:3 to 3:1, by volume. The sequence of utilization of this manganese compound(s) selective sulfur adsorbent in the sequential sulfur adsorbent bed system is preferably for the zeolite sulfur adsorbent to be placed prior to the manganese compound(s) selective sulfur 15 adsorbent. In addition to the use of the manganese compound(s) and the zeolite adsorbent, other selective sulfur adsorbents described herein may be utilized prior to or after the manganese compound(s) selective sulfur adsorbent in the sequential sulfur adsorbent bed system of 20 the invention.

An additional selective sulfur adsorbent, that can be utilized with the zeolite adsorbent in the sequential sulfur adsorbent bed system, comprises copper oxide with alumina, wherein the quantity of the copper oxide is from 5 to 25%, 25 preferably from 10 to 20%, by weight, and the quantity of the alumina is from 75 to 95%, preferably from 80 to 90%, by weight. The surface area of this selective sulfur adsorbent is from 100 to 300 m²/g and preferably from 150 to 300 m²/g.

5 This selective sulfur adsorbent is prepared by conventional procedures.

This selective sulfur adsorbent when used alone has shown particularly usefulness for the adsorption of hydrogen sulfide, carbonyl sulfide, tertiary butyl mercaptan, ethyl
10 mercaptan and mixtures thereof. In addition, this copper oxide with alumina selective sulfur adsorbent, when utilized in sequence with the zeolite adsorbent in the sequential sulfur adsorbent bed system, has shown significant adsorption for sulfur compounds contained in fuel cell feed
15 streams of the same type as are described above. When used in the sequential sulfur adsorbent bed system for the adsorption of sulfur compounds with the zeolite adsorbent, the ratio of the selective sulfur adsorbent to the zeolite adsorbent is from 1:4 to 4:1, preferably from 1:3 to 3:1, by
20 volume. The sequence of utilization of this selective sulfur adsorbent with the zeolite adsorbent in the sequential sulfur adsorbent bed system is preferably for the zeolite adsorbent to be placed prior to the selective sulfur adsorbent. Other selective sulfur adsorbents may also be
25 utilized with this selective sulfur adsorbent for the absorption of sulfur compounds in the sequential sulfur adsorbent bed system of the invention.

An additional selective sulfur adsorbent, that can be

5 utilized with the zeolite adsorbent in the sequential
adsorbent bed system, comprises copper oxide, zinc oxide and
alumina, with the quantity of copper oxide being from 15 to
25%, the quantity of the zinc oxide being from 5 to 15%, and
the quantity of the alumina being from 65 to 85%, by weight.
10 The surface area of this selective sulfur adsorbent is from
100 to 300 m²/g, preferably from 150 to 300 m²/g. This
selective sulfur adsorbent catalyst is prepared by
conventional procedures.

This selective sulfur adsorbent when used alone is
15 particularly useful for the adsorption of hydrogen sulfide,
carbonyl sulfide, tertiary butyl mercaptan, ethyl mercaptan,
and mixtures thereof.

When used with the zeolite adsorbent, the preferred
ratio of this selective sulfur adsorbent with the zeolite
20 adsorbent is from 1:4 to 4:1 and preferably from 1:3 to 3:1,
by volume. The sequence of use of this selective sulfur
adsorbent with the zeolite adsorbent is preferably for the
zeolite adsorbent to be placed prior to the selective sulfur
adsorbent. This selective sulfur adsorbent may be utilized
25 with other selective adsorbents as well as with the zeolite
adsorbent and is a particularly preferred option, as
discussed above. For example, in one particularly preferred
embodiment, this selective sulfur adsorbent is utilized with

5 the zeolite adsorbent and with the iron oxide, manganese compounds and alumina selective sulfur adsorbent, as previously described.

The inventors have surprisingly discovered that the selective sulfur adsorbents described above work best when
10 utilized within a sequential sulfur adsorbent bed system containing one or more of the selective sulfur adsorbents and the zeolite adsorbent. While several types of ion exchanged zeolites may be useful as the zeolite adsorbent, the preferred ion exchange zeolite is a calcium exchanged
15 zeolite. While a number of calcium exchanged zeolites are known, including calcium exchanged zeolite A, zeolite X, zeolite Y, zeolite ZSM-5, zeolite Beta, synthetic mordenite and blends thereof, the preferred calcium exchanged zeolite is a calcium exchanged zeolite X. A particularly preferred
20 calcium exchanged zeolite X is calcium exchanged, low silica zeolite X, known as "LSX", or calcium exchanged low silica faujasite, known as "LSF". Zeolite X generally has a Si:Al equivalent ratio of 1.0 to 1.25. In one common example, a conventional, non-calcium exchanged precursor synthesized
25 LSF has the following anhydrous chemical composition: $2.0 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : 0.73 \text{ Na}_2\text{O} : 0.27 \text{ K}_2\text{O}$, although the ratio between sodium and potassium cations can vary, sometime significantly, depending upon the process of manufacture of

5 the LSF.

For the present invention, a substantial percentage of the cations of the zeolite X are ion exchanged with calcium ions using conventional ion exchange procedures, such as by treatment of the zeolite X with calcium salts, such as, but
10 not limited to, calcium chloride. Several methods can be used for the ion exchange procedure with ion exchange preferably occurring after the zeolite adsorbent has been formed into its preferred final form, such as a bead or an extrudate. The zeolite X is ion exchanged to a level of at
15 least 50%, preferably at least 60%, more preferably at least 70%, and most preferably 85 to 95% of the exchangeable metal ions. The remaining ions may be sodium and/or potassium ions. (For reference purposes the term "calcium exchanged zeolite X" means a zeolite X containing at least about 50%
20 calcium cations.)

The calcium exchanged zeolite X of the invention generally contains sodium or potassium ions in addition to the calcium ions after the calcium ion exchange. However, a portion or substantially all of these sodium/potassium ions
25 can be ion exchanged with other cations to enhance or modify the performance characteristics of the calcium exchanged zeolite X, especially for sulfur adsorption. For example, additional cations that may be ion exchanged onto the

5 zeolite X to enhance its performance include zinc, cadmium, cobalt, nickel, copper, iron, manganese, silver, gold, scandium, lithium and combinations thereof. The percentage of ion exchange of these additional metal ions can range from as little as 1% up to 40% or so, depending upon the
10 level of calcium exchange of the zeolite X. The particular metal ions that are ion exchanged onto the calcium exchanged zeolite depend on the particular sulfur compounds which are intended to be removed from the fuel cell fuel stream by the sequential sulfur adsorbent bed system of the invention.

15 The calcium exchanged zeolite, when utilized above as a sulfur adsorbent, has shown significant capability for the adsorption of various sulfur materials, particularly tetra hydro thiophene (THT), di-methyl sulfide (DMS), tertiary butyl mercaptan (TBM) and ethyl mercaptan (EM).

20 In addition, it has been surprisingly discovered that the capability of the selective sulfur adsorbents described above, when used individually, and the calcium exchanged zeolite, when used individually, can be enhanced dramatically by the combination use of the calcium exchanged
25 zeolite X with the selective sulfur adsorbents to form the sequential sulfur adsorbent bed system for the desulfurization of a hydrocarbon fuel cell feed stream. The use of this combination of the selective sulfur adsorbent

5 with the calcium exchanged zeolite permits the adsorption of
a broader range of sulfur containing compounds than has been
conventionally been adsorbed using either component alone.
For example, it has been surprisingly discovered that by the
use of the selective sulfur adsorbents mentioned above in
10 combination with the calcium exchanged zeolite X described
above, enhanced sulfur adsorption of a broader range of
sulfur compounds, including carbonyl sulfide, hydrogen
sulfide, tetra hydro thiophene, dimethyl sulfide, and
various mercaptans, including ethyl, methyl, propyl, and
15 tertiary butyl mercaptan and combinations thereof, is
possible.

It has also been surprisingly discovered that the
breakthrough time for all sulfur compounds commonly present
in a hydrocarbon fuel system can be extended by the use of
20 one or more selective sulfur adsorbents with the calcium
exchanged zeolite X and by arranging the order of the
components correctly within the sequential sulfur adsorbent
bed system.

It has also been surprisingly discovered that by
25 placement of the calcium exchanged zeolite X prior to one or
more of the selective sulfur adsorbents in the sequential
sulfur adsorption bed system, the likelihood of the
production of synthesized sulfur compounds is substantially

5 reduced.

The inventors have also surprisingly discovered that the sequential sulfur adsorbent bed system of the invention can be utilized at temperatures lower than normally utilized for conventional sulfur adsorption. While conventional
10 chemical sulfur adsorbents require temperatures of the feed stream of at least 150°C to 400°C, the sequential sulfur adsorbent bed system of the invention can be utilized effectively to adsorb the sulfur contaminants at temperatures below 100°C and is effective for removal of
15 some sulfur compounds at temperatures as low as ambient temperatures. Further, because of the lower temperature of use, the sequential sulfur adsorption bed is easier to use than when higher temperatures are necessary.

In addition, when the sequential sulfur adsorbent bed
20 system of the invention is used, the pressure on the feed stream may be reduced to a range as low as from 1 bar to 18 bar, preferably from 1.7 bar to 7 bar, pressures lower than normally used for adsorption of sulfur compounds in a conventional fuel cell processing train.

25 The inventors have also discovered a method for supplying a substantially desulfurized hydrocarbon fuel stream to a fuel cell processor using the sequential sulfur adsorbent bed system described above. In this process a

5 sulfur contaminated hydrocarbon fuel stream is passed over or through the sequential sulfur adsorbent bed system of a fuel cell processor of the invention at a temperature from about ambient to 100°C, preferably less than 60°C, and more preferably at ambient temperatures. By passing a
10 hydrocarbon fuel stream comprising, for example, natural gas, propane or LPG, containing sulfur components at levels up to 500 ppm, a substantial reduction in the quantity of those sulfur compounds, preferably down to a level of less than about 50 ppb, can be achieved.

15 The inventors have also discovered that the above-described sequential sulfur adsorbent bed system of the invention can be used in a desulfurizer, particularly for use in a fuel cell processing train. This desulfurizer includes an inlet for receiving the nondesulfurized
20 hydrocarbon fuel stream, such as natural gas, propane or LPG, the sequential sulfur adsorbent bed system of the invention, as described above, which is placed in a location to desulfurize the hydrocarbon fuel stream, and an outlet where the desulfurized hydrocarbon fuel stream is passed
25 down stream for further processing. For example, the desulfurized hydrocarbon fuel stream can be passed through the fuel cell processing train to the fuel cell stack for

5 the production of electricity.

The inventors have also surprisingly discovered that this method for supplying a substantially desulfurized hydrocarbon fuel stream is more advantageous than conventional desulfurization systems as it permits
10 desulfurization of a broader range of sulfur compounds, increases the breakthrough time for the system, reduces the production of synthesized sulfur compounds, reduces the required temperature and pressure of the feed stream and permits the choice of different combinations and quantities
15 of selective sulfur adsorbents to be used in the sequential sulfur adsorbent bed system depending on the sulfur compounds that are present in the particular feed stream. The compositions and methods of the invention also permit the production of a substantially desulfurized hydrocarbon
20 fuel stream to levels of sulfur below those of conventional desulfurizing processes.

The inventors have also discovered that the sequential sulfur adsorbent bed system of the invention can be used in fuel cell processors for a longer period of time than
25 conventional adsorbents and still achieve high levels of sulfur absorbency.

The inventors have also discovered that the sequential sulfur adsorbent bed system of the invention is also not

5 subject to desorption of the adsorbed sulfur compounds when the conditions surrounding the catalyst bed change, as often occurs with some conventional sulfur adsorbents.

EXAMPLES

The following examples are intended to be illustrative
10 of the present invention and to teach one of ordinary skill in the art to make and use the invention. These examples are not intended to limit the invention in any way.

In order to illustrate the operation of the invention, the inventors have compared the performance of various
15 sulfur adsorbents, when used alone and in combination. In each example, a synthetic natural gas feed stream is utilized comprising 93% methane, 3% ethane, 2% propane, 0.2% butane, 1% carbon dioxide and 0.75% nitrogen. Also included in this synthetic natural gas is 10 ppm (as sulfur) of each
20 of either tert-butyl mercaptan or ethyl mercaptan ("mercaptan") and tetra hydro thiophene ("THT"). This synthetic natural gas is passed through an artificial reactor containing 10 cc of the selected sulfur adsorbent or adsorbents in a bed. When two sulfur adsorbents are used in
25 combination, the quantity of the adsorbents is 7.5 cc of the zeolite sulfur adsorbent, as described in Example 1, and 2.5 cc of the selective sulfur adsorbent, as described in Example 2. The zeolite adsorbent is in the form of 2 mm

5 spheres. The selective sulfur adsorbent is a 1.18 mm x 0.85 mm mesh particulate typically produced from 1.6 mm extrudates by grinding. The adsorbents are sized and loaded into the reactor and the synthetic natural gas feed stream is passed through the reactor. The temperature of the feed stream is maintained at 38°C with a space velocity of 1500 hr⁻¹ at a pressure of 2 bar. "Breakthrough" for this test occurs when greater than 50 ppb of sulfur is observed in the natural gas feed stream after passage through the adsorbent bed. To determine the gas phase sulfur level of the feed stream, analysis was performed using an Agilent 6890 gas chromatograph attached to an Antek 7090 sulfur analyzer. The gas chromatograph utilizes a 60 m X 320 micron DB-1 capillary column for sulfur compound separation. The Antek 7090 utilizes a sulfur chemiluminescence detector (SCD) for sulfur detection. The operational detection limit for the system is approximately 50 ppb (mole). The test unit is controlled by automation software.

Example 1

The synthetic natural gas containing mercaptan and THT is passed through a reactor containing only calcium exchanged zeolite X. The zeolite X has an Si:Al equivalent ratio of 1.17 and a calcium exchange of 70% with the remaining metal ions comprising sodium and/or potassium.

5 The temperature of the reactor is maintained at 38°C and the pressure is maintained at about 2 bar. The sulfur adsorbency of the calcium exchanged zeolite is shown in Figure 1, which shows a first breakthrough for the mercaptan at 268 hours.

10 **Example 2**

The synthetic natural gas containing mercaptan and THT is passed through a reactor containing only a selective sulfur adsorbent comprising 34% by weight manganese compounds, 54% iron oxide comprising Fe₂O₃ and 12% alumina
15 with a surface area of 294 m²/g. The performance of this selective sulfur adsorbent is shown in Figure 2, wherein the first breakthrough occurs at less than 25 hours. The sulfur compound(s) that is produced at that time is a "synthesized sulfur compound" as the breakthrough for THT does not occur
20 until after 100 hours. It is believed that the "synthesized sulfur compounds" is at least one higher molecular weight sulfur compound produced from the interaction of the THT and/or the mercaptan with the selective sulfur adsorbent.

Example 3

25 A further test was run wherein the calcium exchanged zeolite of Example 1 is used in combination with the selective sulfur adsorbent of Example 2 in the reactor. Seventy-five percent of the sulfur adsorbents by volume

5 comprised the zeolite and 25% comprised the selective sulfur
adsorbent. 10 ccs of the combined adsorbents are used. The
zeolite was placed ahead of the selective sulfur adsorbent
in the reactor. Otherwise, the operating conditions and the
composition of the feed stream are the same as for Examples
10 1 and 2. When the feed stream is passed through the
reactor, breakthrough does not occur until 496 hours as
shown in Figure 3.

As is clear from these examples, the combination of the
calcium exchanged zeolite with the selective sulfur
15 adsorbent increases the time of sulfur breakthrough,
prevents the formation of synthesized sulfur compounds and
extends the lifetime of the sequential sulfur adsorbent bed
system.

As many changes and variations in the disclosed
20 embodiments may be made without departing from the inventive
concept, the invention is not intended to be limited.

5 **Claims**

Claim 1. A process for desulfurization of a hydrocarbon feed stream comprising

providing a hydrocarbon feed stream, which is
10 contaminated with sulfur compounds,

passing the sulfur contaminated feed stream through a sequential sulfur adsorbent bed system comprising a selective sulfur adsorbent and a calcium exchanged zeolite sulfur adsorbent, preferably a calcium exchanged zeolite X
15 or LSX, wherein the calcium exchanged zeolite is exchanged with calcium ions at least 50%, preferably at least 70% and more preferably from 85 to 95% of the exchangeable metal ions, to produce a hydrocarbon feed stream, which has been substantially desulfurized.

20 Claim 2. The process of Claim 1, wherein the temperature of the sequential sulfur adsorbent bed system, as the feed stream passes therethrough, is from ambient to 100°C.

Claim 3. The process of any of Claims 1 or 2, wherein
25 the selective sulfur adsorbent comprises a manganese-based sulfur adsorbent.

Claim 4. The process of any of Claims 1 or 2, wherein the selective sulfur adsorbent is selected from the group

5 consisting of substantially ZnO; CuO and carbon; CuO, ZnO and a carrier; and CuO and an alumina and mixtures thereof.

Claim 5. The process of any of Claims 1 or 2, wherein the selective sulfur adsorbent comprises CuO, a manganese compound and a binder.

10 Claim 6. The process of any of Claims 1 or 2, wherein the selective sulfur absorbent comprises a manganese compound, an iron compound and high surface area alumina.

Claim 7. The process of any of Claims 1-6, wherein the calcium exchanged zeolite is further ion exchanged with
15 metal ions selected from the group consisting of zinc, cadmium, cobalt, nickel, copper, iron, manganese, silver, gold, scandium, lithium and combinations thereof, preferably from 1% to 40% of the available metal ions.

Claim 8. The process of any of Claims 1-7, wherein the
20 feed stream contacts the calcium exchanged zeolite prior to contacting the selective sulfur absorbent.

Claim 9. A process for the desulfurization of a hydrocarbon fuel cell feed stream comprising

providing the hydrocarbon feed stream to a fuel cell
25 processing train, wherein the feed stream is contaminated with sulfur compounds including one or more compounds selected from the group consisting of carbonyl sulfide, hydrogen sulfide, tetra hydro thiophene, dimethyl sulfide,

5 mercaptans, disulfides, thiophenes, sulfoxides, other organic sulfides, and higher molecular weight organic sulfur compounds and combinations thereof,

passing the sulfur contaminated feed stream through a sequential sulfur adsorbent bed system comprising a calcium
10 exchange zeolite X, wherein the calcium exchanged zeolite X is preferably exchanged with calcium ions at least 50%, more preferably at least 70% and most preferably from 85 to 95% of the exchangeable metal ions, and a manganese-based selective sulfur adsorbent to produce a hydrocarbon feed
15 stream which has been substantially desulfurized, and

delivering the substantially desulfurized hydrocarbon feed stream to remaining components of the fuel cell system.

Claim 10. The process of Claim 9, wherein the temperature of the sequential sulfur adsorbent bed system as
20 the feed stream passes therethrough is from ambient to 100°C.

Claim 11. A sequential adsorbent bed system for use in a fuel cell processing train comprising a selective sulfur adsorbent and a calcium exchanged zeolite, wherein the
25 selective sulfur adsorbent comprises one or more manganese compounds selected from the group consisting of MnO_2 , Mn_2O_3 , Mn_3O_4 and $\text{Mn}(\text{OH})_4$ and mixtures thereof, iron oxide, and a high surface area support, and wherein the calcium exchanged

5 zeolite comprises a calcium exchanged zeolite X, ion
exchanged to at least 50% of the available metal ions with
calcium ions, more preferably ion exchanged at least 70%,
and most preferably ion exchanged from 85 to 95% of the
exchanged metal ions with calcium ions.

10 Claim 12. A sequential adsorbent bed system for use in
a fuel cell processing train comprising a selective sulfur
adsorbent and a calcium exchanged zeolite, wherein the
calcium exchanged zeolite comprises a calcium exchanged
zeolite X, ion exchanged to at least 50% of the available
15 metal ions with calcium ions, more preferably ion exchanged
at least 70%, and most preferably ion exchanged from 85 to
95% of the exchangable metal ions with calcium ions, and
wherein the selective sulfur adsorbent comprises one or more
manganese compounds selected from the group consisting of
20 MnO_2 , Mn_2O_3 , Mn_3O_4 and $\text{Mn}(\text{OH})_4$ and mixtures thereof, copper
oxide and a binder.

Claim 13. A sequential adsorbent bed system for use in
a fuel cell processing train comprising two selective sulfur
adsorbents and a calcium exchanged zeolite, wherein the
25 calcium exchanged zeolite comprises a calcium exchanged
zeolite X, ion exchanged to at least 50% of the available
metal ions with calcium cations, more preferably ion
exchanged at least 70%, and most preferably ion exchanged

5 from 85 to 95% of the exchangeable metal ions with calcium ions, and wherein a first of the two selective sulfur adsorbents comprises one or more manganese compounds selected from the group consisting of MnO_2 , Mn_2O_3 , Mn_3O_4 and $\text{Mn}(\text{OH})_4$ and mixtures thereof, iron oxide and a high surface
10 area support and wherein a second of the two selective sulfur adsorbents comprises copper oxide and activated carbon.

Claim 14. A sequential adsorbent bed system comprising two selective sulfur adsorbents and a calcium exchanged
15 zeolite, wherein the calcium exchanged zeolite comprises a calcium exchanged zeolite X, ion exchanged to at least 50% of the available metal cations with calcium cations, more preferably ion exchanged at least 70%, and most preferably ion exchanged from 85 to 95% of the exchangeable metal ions
20 with calcium ions, wherein the first of the two selective sulfur adsorbents comprises one or more manganese compounds selected from the group consisting of MnO_2 , Mn_2O_3 , Mn_3O_4 and $\text{Mn}(\text{OH})_4$ and mixtures thereof, iron oxide and a high surface area support, and wherein a second of the two selective
25 sulfur adsorbents comprises zinc oxide, copper oxide and alumina.

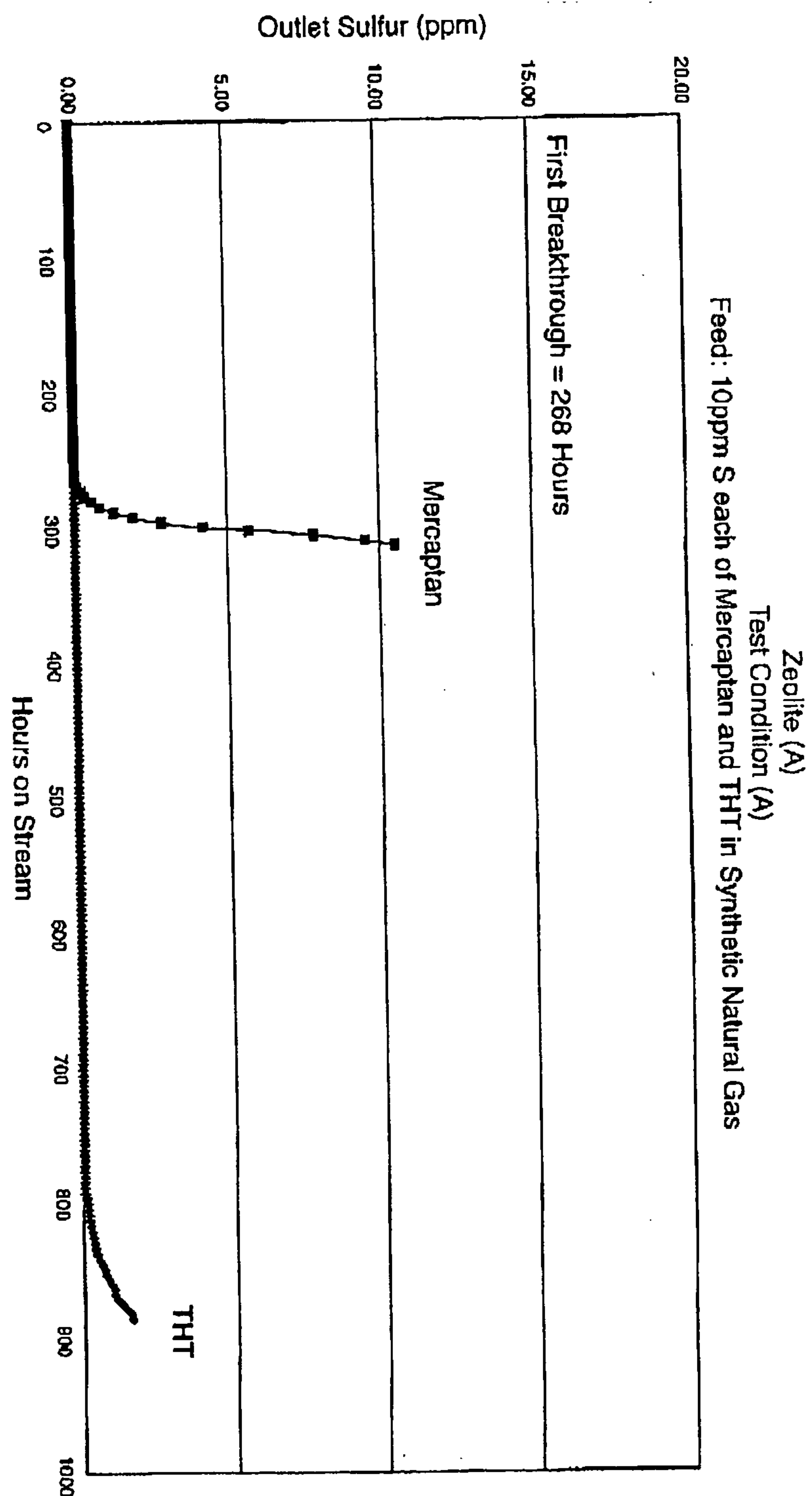


Fig. 1

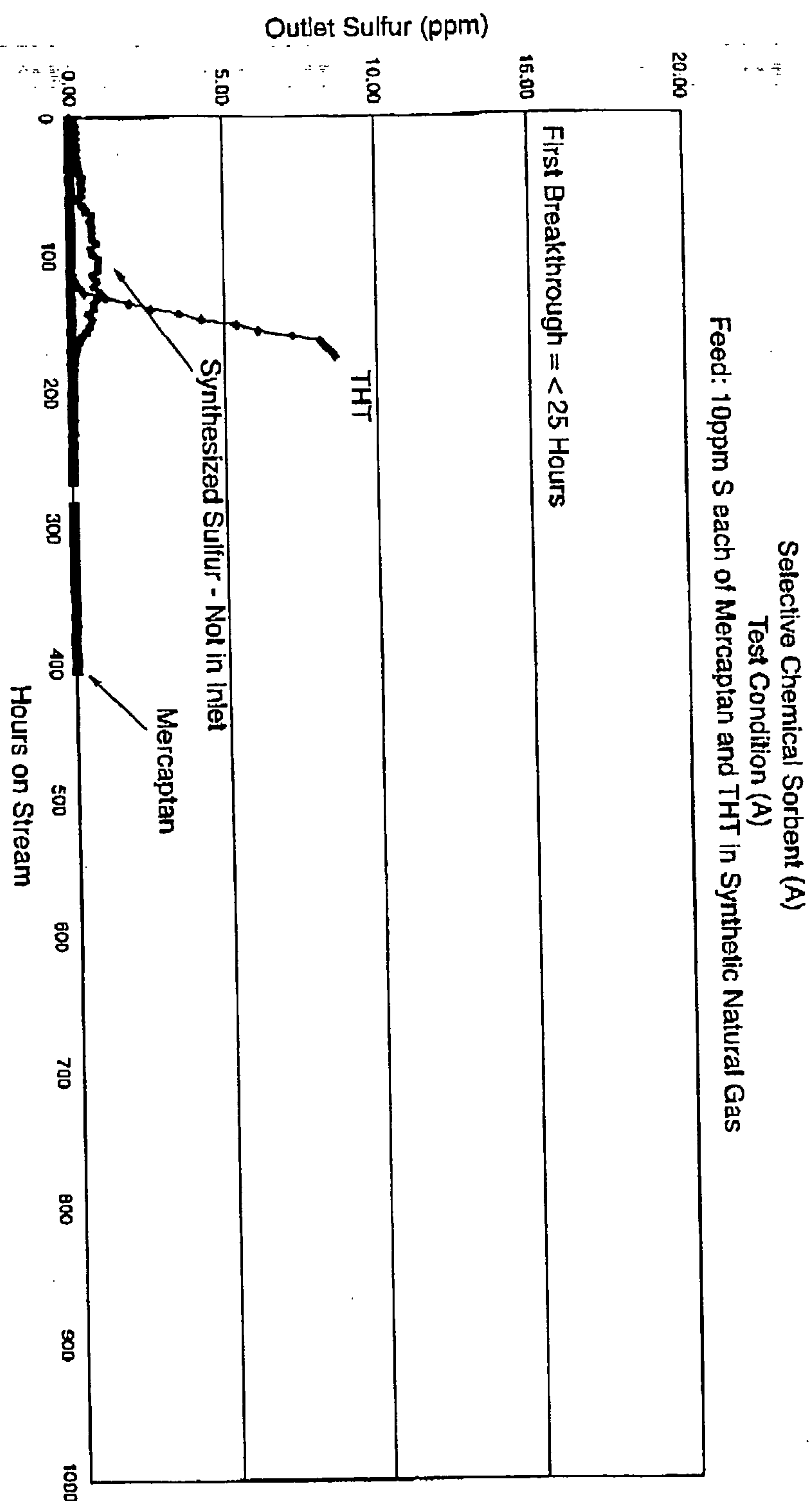


Fig. 2

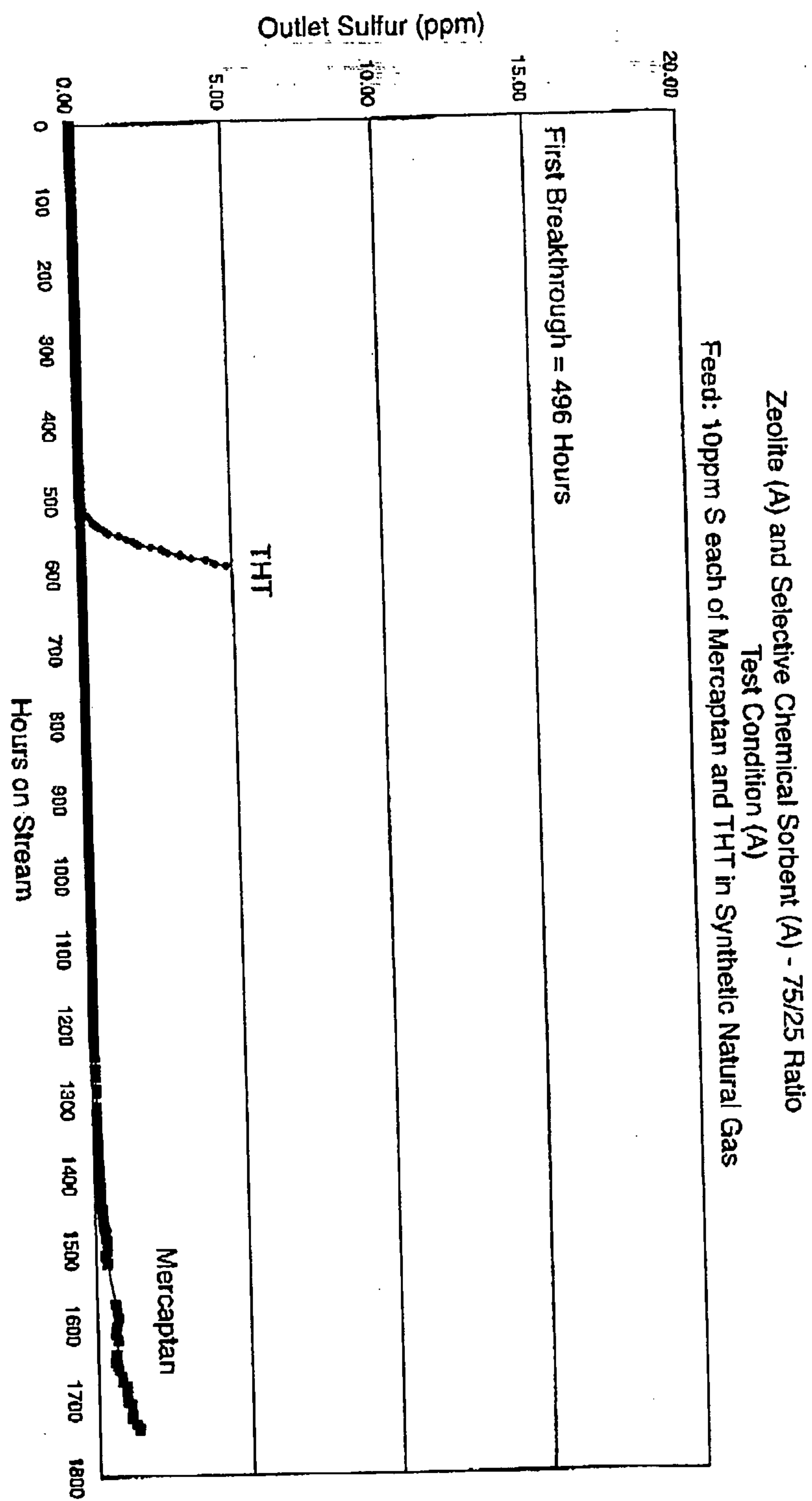


Fig. 3

Zeolite (A) and Selective Chemical Sorbent (A) - 75/25 Ratio

Test Condition (A)

Feed: 10ppm S each of Mercaptan and THT in Synthetic Natural Gas

