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CATALYTIC-CARTRIDGE SO<sub>3</sub> DECOMPOSER

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## SO<sub>3</sub> DECOMPOSER

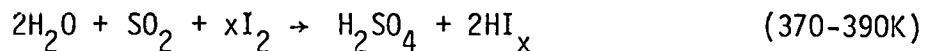
### Background of the Invention

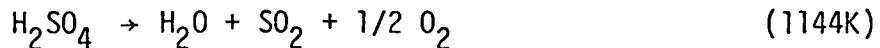
The invention relates to thermochemical cycles for hydrogen production and more particularly to sulfur trioxide (SO<sub>3</sub>) decomposition reactors utilized in thermochemical cycles for hydrogen production. The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-48 between the U.S. Department of Energy and the University of California.

This application is a continuation in part of U.S. patent application serial number 208,218, filed November 18, 1980, for "Catalytic Cartridge SO<sub>3</sub> Decomposer".

Hydrogen, a valuable raw material for the petroleum and petrochemical industries, is expected to become by early in the next century an important renewable-based, transportable fuel either by itself or in some hydrocarbon form such as methanol. Hydrogen can be produced through the decomposition of water by means of thermochemical cycles which reduce the high temperature requirements of the 3000K (degrees Kelvin) straight thermal decomposition process to the 1200K levels that can be generated in nuclear fission or fusion reactors or in high intensity, focused solar reflectors.

An example of a thermochemical process for producing hydrogen is the sulfur-iodine cycle being developed by the General Atomic Company. The essential steps of the sulfur iodine cycle are represented by the following reactions:





The dominant energy requirements, heat versus temperature, are necessary in this process for the  $\text{H}_2\text{SO}_4$  concentration and vaporization, conversion of  $\text{H}_2\text{SO}_4$  into  $\text{SO}_3 + \text{H}_2\text{O}$ , and  $\text{SO}_3$

5 decomposition steps.

The  $\text{SO}_3$  decomposer is the critical process unit in nearly all the viable thermochemical plants to produce hydrogen. These plants can be driven by high temperature gas reactors, solar collectors or fusion reactors, utilizing sodium, potassium or helium as heat transfer fluids

10 to supply the large heat demand of the  $\text{SO}_3$  decomposer. Catalysts are required in the decomposer in order to keep the temperature required to reasonable levels of 1070-1120K. The key requirement is to supply heat to the catalytic surfaces where the endothermic  $\text{SO}_3$  reaction occurs. This  $\text{SO}_3$  decomposition produces  $\text{SO}_2$  and  $\text{O}_2$  for the thermochemical

15 production of hydrogen.

Measured  $\text{SO}_3$  kinetics and equilibrium show this high temperature  $\text{SO}_3$  decomposition reactor to be surface kinetics (heterogeneous) controlled at lower temperatures, below 1050K, and homogeneous at higher temperatures, above 1180K. For non-catalytic

20 surfaces the conversion from  $\text{SO}_3$  to  $\text{SO}_2$  is about 20-30% over the temperature range 1080K to 1180K for a 0.3 to 1 second residence time at around 1.5 atm. total pressure. The low conversion leads to large recycle  $\text{H}_2\text{SO}_4$  flows and thus much larger and more expensive equipment. Increased residence time improves the kinetics but

25 increases the size of the equipment. Increased total pressure decreases the equipment size but unfavorably shifts the equilibrium, and decreased conversion increases equipment size. Catalytically enhanced kinetics greatly improve the conversion to the range of 65-80%. It is desirable to operate at a temperature of around 1050K in

30 order to eliminate the need of very expensive platinum catalysts and allow substitution of much less expensive  $\text{CuO}$  or  $\text{Fe}_2\text{O}_3$  catalysts.

The design of a chemical reactor with fast kinetics and large associated heat effects is very difficult. A design of least cost and greatest simplicity is desired. Catalytic decomposers heated by

internal heat exchangers appear to be too large to be cost competitive with other hydrogen production technologies. The most obvious choice, a packed bed reactor, does not appear feasible because heat transfer from in-bed heat exchangers to the packed bed of catalysts is very 5 inefficient and requires extremely large temperature gradients between the heat exchanger fluid and the packed bed. Costly, high heat transfer media flow rates are also required, and large radial temperature gradients appear within the bed between the internal heat 10 exchanger tube elements. Fluidization of the bed of catalysts greatly reduces the temperature differences between the heat transfer fluid and the catalyst surface. However, substantial pumping power is required 15 to fluidize the bed, resulting in a higher operational cost design.

Fusion reactors offer some unique advantages as drivers for thermochemical hydrogen plants. Thermal heat from the blanket of a 20 tandem mirror fusion reactor can be utilized. One particular tandem mirror blanket concept is a lithium-sodium, liquid metal 50% weight mixture in the cauldron blanket module. Helium or sodium can be used as the heat transfer fluid to carry heat outside the nuclear island to process exchangers within the thermochemical hydrogen production 25 cycle. Either a direct condensing vapor heat exchange loop or a heat pipe driven loop can be utilized. Problems with this design, however, include the safety problems of the isolation of liquid metals from the process stream and the permeation of radioactive tritium into the product stream.

Thermochemical cycles, the interface with thermal reactors, fluidized bed decomposer designs, and associated problems, are 30 described in UCRL-84212, "Interfacing the Tandem Mirror Reactor to the Sulfur Iodine Process for Hydrogen Production", T.R. Galloway, Lawrence Livermore National Laboratory, June 1980, and UCRL-84285, "The Process Aspects of Hydrogen Production Using the Tandem Mirror Reactor", T.R. Galloway, Lawrence Livermore National Laboratory, September 1980, which are herein incorporated by reference.

It is accordingly an object of the invention to provide a low cost and high efficiency  $\text{SO}_3$  decomposer for a thermochemical hydrogen 35 production process.

It is also an object of the invention to provide a catalytic  $\text{SO}_3$  decomposer which can be interfaced with a tandem mirror fusion reactor at 1200K or below.

5 It is another object of the invention to provide a  $\text{SO}_3$  decomposer with improved safety barriers and added modularity for increased reliability.

It is also an object of the invention to provide a  $\text{SO}_3$  decomposer which can interface with a fusion reactor which has improved tritium processing and isolation features.

10 It is another object of the invention to provide a  $\text{SO}_3$  decomposer which operates at a temperature to allow the use of inexpensive  $\text{CuO}$  or  $\text{Fe}_2\text{O}_3$  catalysts in place of more expensive platinum catalysts.

15 It is yet another object of the invention to provide a  $\text{SO}_3$  decomposer which provides a high efficiency transfer of heat from the source to the catalyst.

It is still another object of the invention to provide a  $\text{SO}_3$  decomposer which has a high conversion efficiency.

20 Summary of the Invention

The invention is an improved  $\text{SO}_3$  decomposer for thermochemical hydrogen production comprising a cartridge having a surface coated with a catalyst. The catalytic cartridge is internally heated to heat the catalyst, and  $\text{SO}_3$  gas is flowed through the cartridge to contact the catalyst which is heated to a sufficient temperature to produce the  $\text{SO}_3$  decomposition reactions. There are two preferred embodiments of the invention, a cross-flow cartridge and an axial-flow cartridge. In the cross-flow catalytic cartridge, the process gases flow through a chamber and are incident normal to a catalyst coated tube extending 25 through the chamber. In the axial-flow catalytic cartridge, the process gases flow parallel to a catalyst coated tube in an annular space surrounding the catalyst coated tube. The catalyst coated tube of either decomposer design is internally heated by heating means which are mounted inside the catalyst coated tubes to heat the catalyst 30 surface over which the  $\text{SO}_3$  gas flows to sufficient temperatures to 35

produce  $\text{SO}_3$  decomposition into  $\text{SO}_2 + \text{O}_2$ . The catalyst coated tube can be heated by a heat pipe, by electrical heating by neutrons or other particles, by radiative heating, by combustion, by the flow of hot fluids, or by any other heating means or process which can be

5 adapted to the catalytic cartridge. In particular, when a fusion reactor is utilized as the heat source, a tritium-concentrating heat pipe plus counter-current helium purge in a narrow gap between the heat pipe and the catalyst coated tube can be utilized to remove radioactive tritium.

10 The catalytic cartridge having an internal heating means eliminates many of the disadvantages of the prior art. No dangerous sodium or potassium heat transfer fluids are needed. No large temperature differences exist between the heat source and the catalyst surface. No large heat transfer fluid flow rates are required. No 15 high pressure helium gas is necessary. The design provides a very safe system which eliminates the danger of escape of radioactive tritium from a fusion reactor to manned areas.

20 The foregoing and other aspects of the invention will become apparent from the following detailed description in conjunction with the accompanying drawings.

#### Brief Description of the Drawings

Figure 1 is a sectional schematic view of the cross-flow catalytic cartridge decomposer, having a heat pipe for internally 25 heating the catalyst.

Figure 2 is a perspective schematic view of the cross-flow catalytic cartridge decomposer.

Figure 3 is a sectional schematic view of the axial-flow catalytic cartridge decomposer, having a heat pipe for internally 30 heating the catalyst.

#### Detailed Description

The cross-flow catalytic cartridge  $\text{SO}_3$  decomposer 10, shown in Figures 1 and 2, comprises a hermetically sealed process module or

chamber 12 having lateral sides 11 and 13, top side 15, and bottom side 17. A metal alloy tube 14 extends through chamber 12 from lateral side 11 to lateral side 13. The tube 14 is heated by any heating means placed in the tube or any heating method carried out in the tube. As 5 an illustrative embodiment, shown in Figure 1, the tube 14 surrounds the condenser region 16 of a heat pipe 20. The evaporator region 18 of heat pipe 20 is exposed to a heat source such as a fusion reactor or solar collector. The heat pipe transports heat from the heat source through the isolating wall 22 to the catalytic cartridge 10. The tube 10 14 extending through the chamber 12 is in thermal contact with the condenser region 16 of heat pipe 20 or is separated from the condenser region 16 by a narrow gap 26. A layer 24 of catalyst is coated on the tube 14 and is heated by heat transfer from the heat pipe 20, being kept at a temperature of about 1070K.  $\text{SO}_3$  gas is flowed in through 15 inlet port 19 at one end of chamber 12 and flowed through the chamber 12 incident to the tube 14 across the heated catalyst layer 24, thereby producing the decomposition reaction of  $\text{SO}_3$ . The decomposition products  $\text{SO}_2 + \text{O}_2$  are removed through outlet port 21 at the opposite end of chamber 12 and are utilized in the thermochemical 20 hydrogen production cycle. The flow of the  $\text{SO}_3$  gas is a cross-flow through the chamber 12 through which the tube 14 extends normal to the gas flow.

The methods and means of internally heating the catalyst coated tubes can include, according to the invention, a heat pipe extending 25 into the catalyst coated tube from any external heat source including the blanket of a magnetic fusion reactor or the core of a fission reactor; an electrical heater placed inside the tube and activated by any source of electrical energy, including a fusion or fission reactor; means to radiatively heat the catalyst by directing neutrons, other 30 particles, x-rays, or other photon energy, from any radiation source, into the tube; means, including combustion tubes, to heat the catalyst by producing any combustion process within the tubes; and flowing any coolant, moderator, or fluid including water, liquid metal, or helium, heated from any fission or fusion reactor, any solar heater, or any 35 other heat source, into the tubes.

When the heat source is a fusion reactor with the attendant problem of radioactive tritium permeation, the heat pipe 20 is a tritium-concentrating heat pipe having a tritium permeable window 28, such as a niobium window, at the end of the condenser region 16

5 farthest from the evaporator region 18. With the fusion reactor heat source, a decomposer design having a gap 26 between the catalytic cartridge tube 14 and the heat pipe 20 is preferable. Helium gas is flowed through the gap 26 to sweep out any tritium which permeates radially out of the heat pipe 20 or through window 28. The flowing

10 helium sweep gas removes all of the permeated tritium through aperture 30 provided in the chamber wall 11.

The cross-flow catalytic cartridge 10 provides a simple design having the lowest capital cost and high performance. The design provides a chamber 12 which is a single modular unit hermetically sealed from the heat pipe 20 and flowing helium gas, or other heating means, for high reliability and safety. The catalyst, for ease of deposition, can cover all of the chamber 12 instead of just the tube 14, particularly when low cost catalysts are used. The design provides significant heat transfer advantages as well. The most efficient heat transfer is obtained when tube 14 makes thermal contact with heat pipe 20 or other heating means. When gap 26 is included, an additional temperature drop between the heat pipe 20 and catalyst layer 24 is introduced. The cross flow around the catalyst coated tube 14 is more effective due to turbulence provided by the wake of the gas flow around the tube which enhances the heat transfer.

The axial-flow catalytic cartridge decomposer 50, shown in Figure 3, comprises a cylindrical cartridge 52 having an inner cylindrical wall or tube 54 and a concentric outer wall or tube 64, defining an annular space 66 therebetween, and joined at end walls 53 and 55. The 30 inner wall or tube 54 is heated by any heating means placed in the tube or any heating method carried out in the tube. As an illustrative embodiment, shown in Figure 3, the tube 54 surrounds the condenser region 56 of heat pipe 58. The surface of the cylindrical wall 54 at the annular space 66 is coated with a layer 62 of catalyst. The 35 evaporator section 60 of heat pipe 58 is exposed to a heat source such

as a fusion reactor, nuclear reactor or solar collector. The heat pipe 58 transports heat from the heat source through the isolating wall 61 to the catalytic cartridge 52. The cylindrical wall 54 is in thermal contact with the condenser region 56 of heat pipe 58 or is separated 5 from the heat pipe by a narrow gap 72. The heat pipe keeps the catalytic layer 62 at a temperature of about 1070K. Process  $SO_3$  gas is flowed into the annular space 66 through inlet 68 located at one end of outer wall 64 and flows axially through the cartridge over the catalytic surface 62 thereby producing decomposition reactions into 10  $SO_2$  plus  $O_2$  which are removed from the cartridge 52 through outlet 70 at the opposite end of outer wall 64. The surface of the outer wall 64 of the annular space can also be coated with catalyst as well as the inner wall 54. The  $SO_3$  gas flow is preferably from the end of the heat pipe condenser region 56 toward the evaporator region 60 so that 15 the counter-flowing gas leaves at the hottest conditions, thereby resulting in the highest conversion.

The methods and means of internally heating the catalyst coated tubes can include, according to the invention, a heat pipe extending into the catalyst coated tube from any external heat source including 20 the blanket of a magnetic fusion reactor or the core of a fission reactor; an electrical heater placed inside the tube and activated by any source of electrical energy including a fusion or fission reactor; means to radiatively heat the catalyst by directing neutrons, other particles, x-rays, or other photon energy, from any radiation source, 25 into the tube; means, including combustion tubes, to heat the catalyst by producing any combustion process within the tubes; and flowing any coolant, moderator, or fluid including water, liquid metal, or helium, heated from any fission or fusion reactor, any solar heater, or any other heat source, into the tubes.

30 When the heat source is a fusion reactor which contains radioactive tritium, the heat pipe 58 is a tritium concentrating heat pipe having a tritium permeable window 74 such as a niobium window at the end of the condenser region 56. When the heat source contains radioactive tritium, the cartridge design having a narrow gap 72 35 between the wall 54 and heat pipe 58 is utilized and helium gas is

flowed through the pipe to sweep out permeated tritium through aperture 76 in end wall 53. Heat pipe technology and the tritium concentrating heat pipe are described in UCRL-50510, "Concept for a Gas-Buffered Annular Heat Pipe Fuel Irradiation Capsule", J.D. Lee and R.W. Werner, 5 Lawrence Livermore National Laboratory, 1968, and UCID-15390, "The Generation and Recovery of Tritium in Thermonuclear Reactor Blankets", R.W. Werner, Lawrence Livermore National Laboratory, 1968, which are herein incorporated by reference.

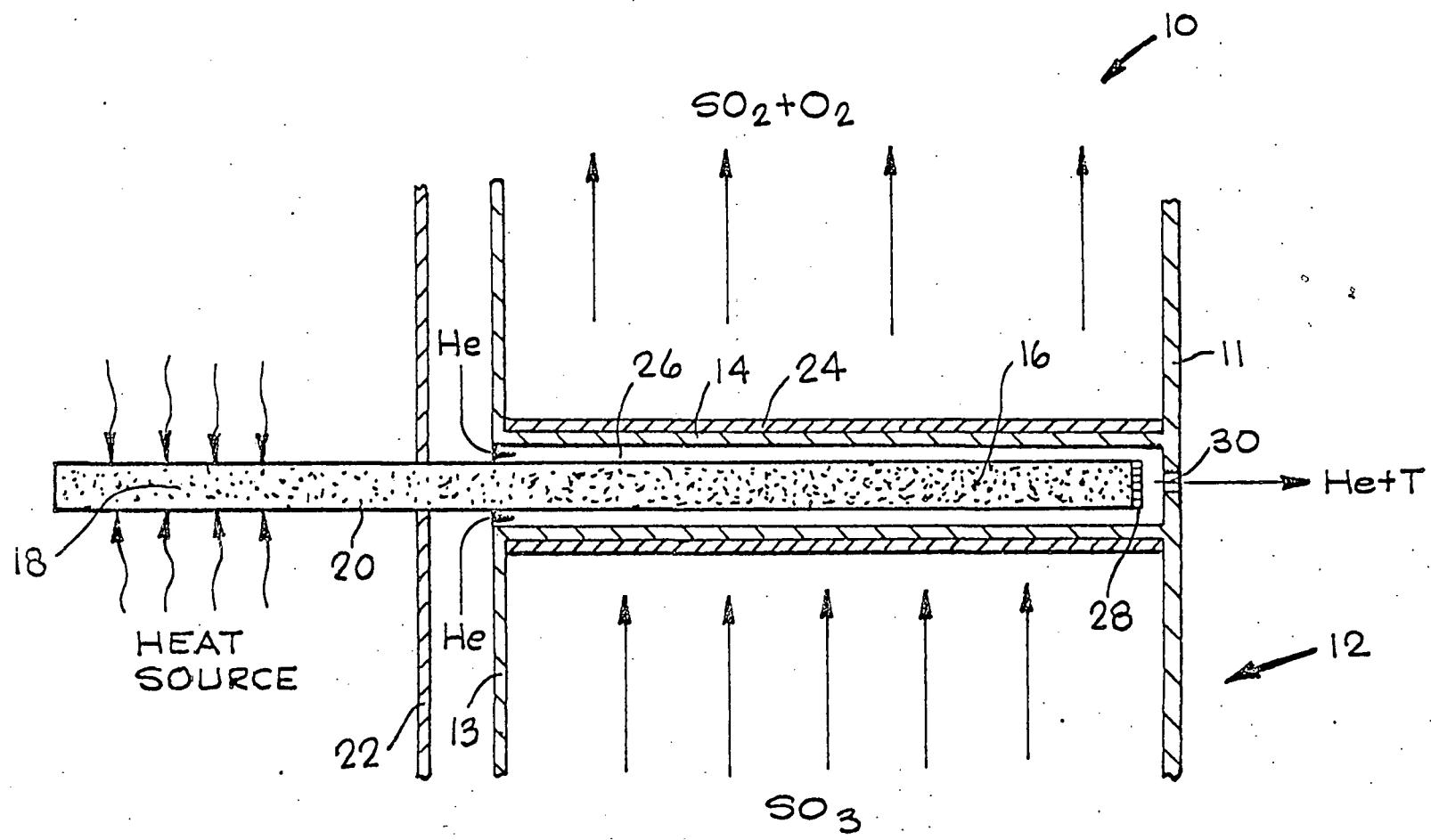
In both cartridge designs, the closeness of the catalytic 10 surface to the heat pipe or other heating means results in a highly efficient heat transfer to the catalyst with a small temperature gradient. The catalytic surface is kept at a temperature of about 1070K by the heat pipe or other heating means to produce the  $\text{SO}_3$  decomposition reactions with a high conversion efficiency. The 15 catalyst is a heavy metal oxide such as  $\text{CuO}$  or  $\text{Fe}_2\text{O}_3$  or a precious metal such as platinum, coated onto alumina, zeolite, silica, or other substrates. The substrates, which are mostly ceramic, can be deposited on the metal surface but high quality thermal contact is not required. The catalytic cartridge is preferably made of a metal alloy such as 20 aluminized Incoloy 800H in order to resist the corrosive  $\text{SO}_2$ . The catalyst coating on the surface is about 250 microns thick. Since the reaction depth is 250 microns, the catalyst layer is therefore fully active. The heat pipe is typically 1 cm in diameter and has a condensing region 2 meters in length. The heat pipe may be made of 25 Incoloy 800H with a wall thickness of 1/2 mm to 1 mm. The heat pipe would operate at around 1120K when the catalyst coated wall is in thermal contact with the heat pipe. The annular gap for helium gas flow is 1/2 mm and introduces a temperature drop of about 70K which might be reduced by using a grooved passageway for the helium gas 30 instead of an annular gap. The helium gas sweep can be at low pressure and rate, under 0.1 m/s and 0.01 atm. With the added temperature drop across the gap, the heat pipe would operate at around 1190K. The  $\text{SO}_3$  process stream enters the catalytic cartridge at 1050K so the decomposer need not supply the sensible heat to raise the  $\text{SO}_3$  from 35 800K to 1050K. A preheater with a similar configuration to the

catalytic cartridge but without any catalytic surfaces could be utilized to preheat the  $\text{SO}_3$ . A combined unit could be utilized in which the heat pipe temperature would be higher in order to simultaneously supply the sensible heat and the endothermic heat of reaction. In a thermochemical plant, a modular array of catalytic cartridges and heat pipes or other heating means could be utilized.

Changes and modifications in the specifically described embodiments can be carried out without departing from the scope of the invention, which is intended to be limited only by the scope of the appended claims.

### Abstract

A catalytic cartridge internally heated is utilized as a  $\text{SO}_3$  decomposer for thermochemical hydrogen production. The cartridge has two embodiments, a cross-flow cartridge and an axial flow cartridge. In the cross-flow cartridge,  $\text{SO}_3$  gas is flowed through a chamber and incident normally to a catalyst coated tube extending through the chamber, the catalyst coated tube being internally heated. In the axial-flow cartridge,  $\text{SO}_3$  gas is flowed through the annular space between concentric inner and outer cylindrical walls, the inner cylindrical wall being coated by a catalyst and being internally heated. The modular cartridge decomposer provides high thermal efficiency, high conversion efficiency, and increased safety.



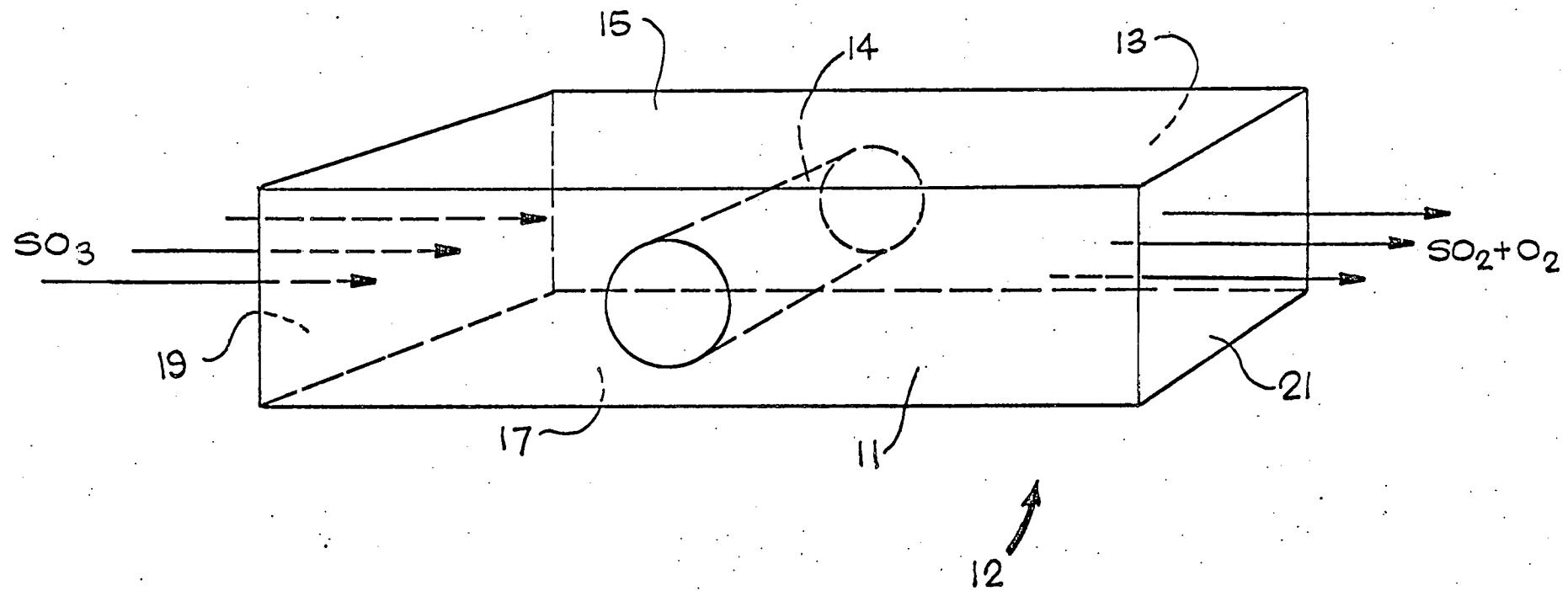
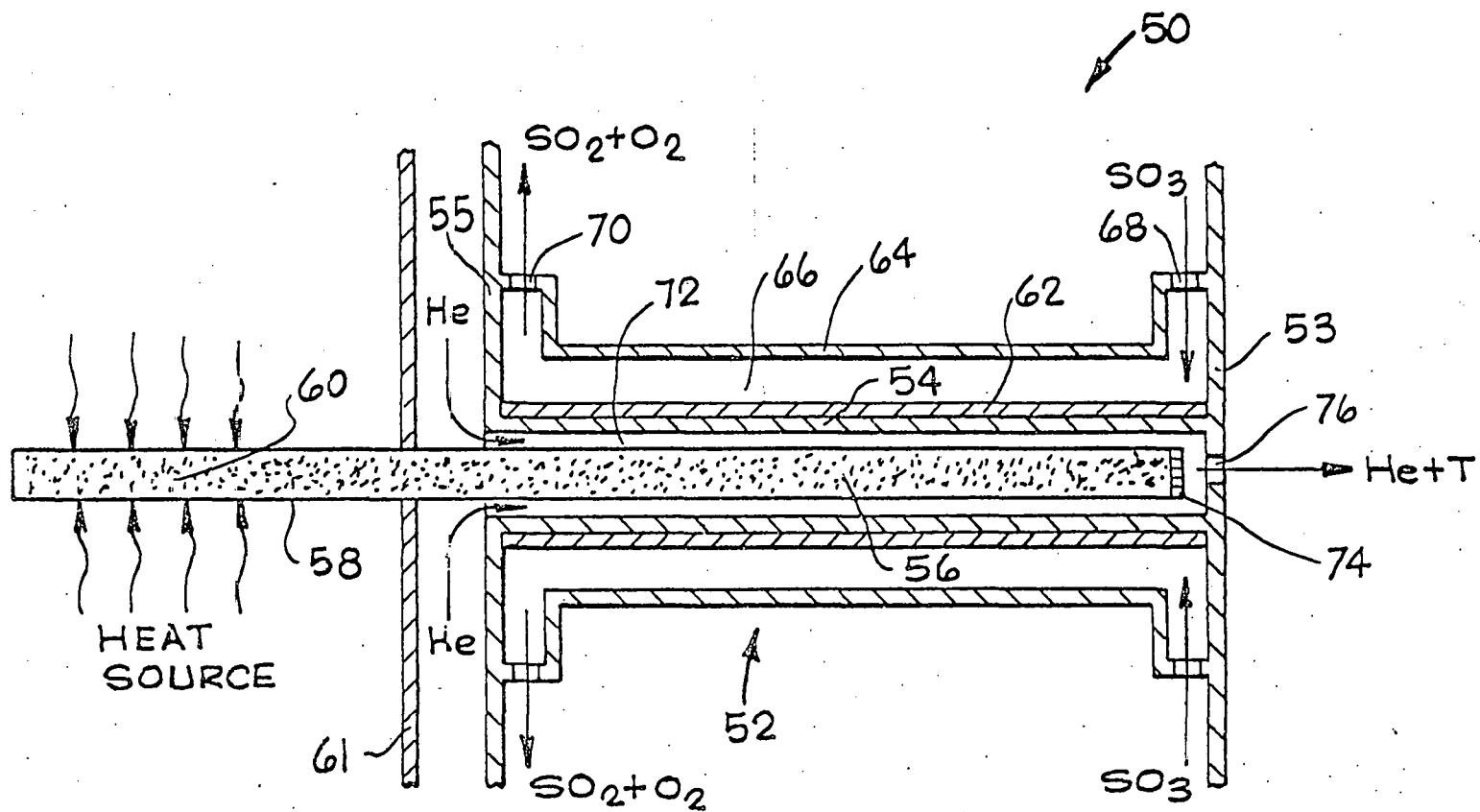


Fig. 2



### Fig. 3