United States Patent

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[54] ELECTROCHEMICAL CELL HAVING A BIPOLAR ELECTRODE

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[52] **U.S. Cl.** ..... **204/248**, 204/78, 204/104, 204/268, 204/277, 204/278, 204/284, 204/290 R, 204/294

[51] **Int. Cl.** **B01k 3/04**, C22d 1/02

[58] **Field of Search** ..... 136/86; 204/248, 249, 268, 204/284, 129, 78, 104, 290 R

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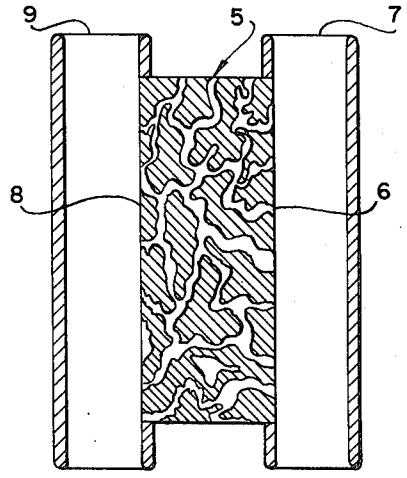
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[57] **ABSTRACT**

An electrochemical cell is disclosed which comprises a bipolar electrode having two spaced surfaces adapted for exposure to an oxidizing agent and a reducing agent, respectively. The two electrode surfaces are interconnected by ion and electron conveyance means. The electrochemical cell may be used in recovering sulfur from flue gases in the form of sulfuric acid of commercial purity and concentration.

1 Claims, 4 Drawing Figures



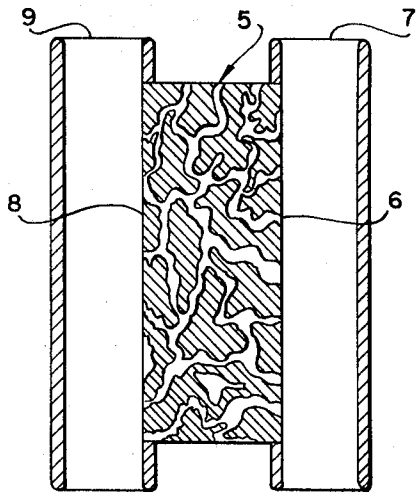


FIG_1

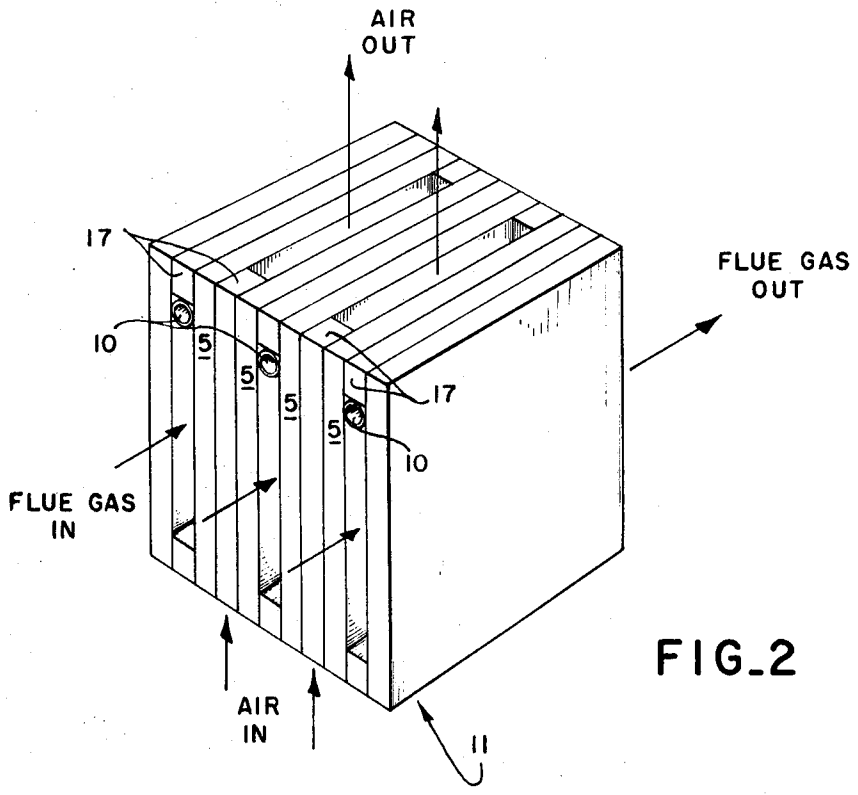
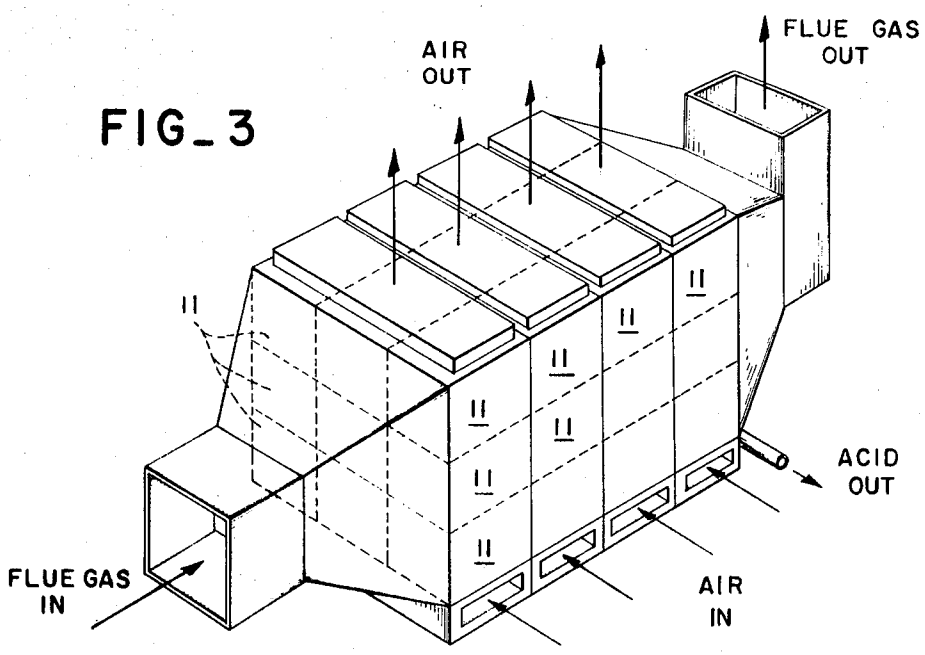


FIG_2

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FIG_3



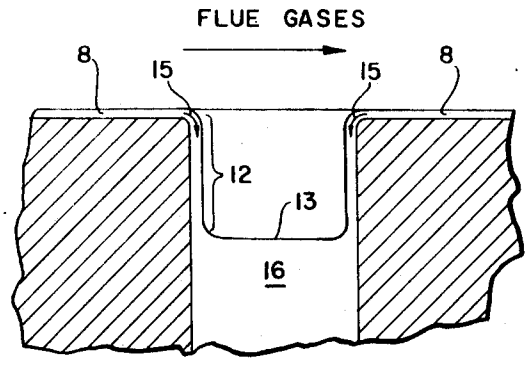


FIG_4

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ELECTROCHEMICAL CELL HAVING A BIPOLAR ELECTRODE

BACKGROUND OF THE INVENTION

This invention relates generally to electrochemical cells of the galvanic type, and particularly to electrochemical means for oxidizing fluids containing oxidizable materials such as sulfur dioxide, ionized iron, formaldehyde, methanol, sugars and sewage. For clarity of expression and explanation sulfur dioxide is hereinafter considered the substance which undergoes oxidation. It should, however, be understood that sulfur dioxide is merely exemplary of materials which may be oxidized in accordance with the teaching of this invention.

The sulfur dioxide content in flue gases is a principal contributor to air pollution. Its removal from flue gases and conversion to a commercially useful form of sulfur, such as sulfuric acid, would obviously be a significant technological achievement if done in an economical manner.

Sulfur dioxide may be removed from flue gases by conversion to a reaction product having little if any market value. The substantial costs of supplying a consumable reactant and of disposing of an unmarketable product renders such a process undesirable, particularly in view of the intrinsic value of sulfur itself. Therefore, those processes which recover sulfur and sulfur products from flue gases in lieu of discarding it are clearly the more valuable. As the principle uses of the element and the dioxide today are for the production of sulfuric acid, a process through which sulfur dioxide would be recovered from flue gases with sufficiently concentrated sulfuric acid being the reaction product would be of unique value.

Heretofore, sulfuric acid has ordinarily been commercially produced by either one of two principal processes, namely the contact process or the chamber process. In the contact process highly purified sulfur dioxide is mixed with air and passed over a platinum catalyzer to form sulfur trioxide which reacts with water to form sulfuric acid. In the chamber process a controlled ratio of carefully prepared sulfur dioxide, water mist and nitrogen oxides are introduced into large lead-lined chambers in forming the acid. Obviously, neither process could effectively use flue gases as their source of sulfur dioxide due to the variant proportions of the dioxide therein plus the presence of the other often unknown materials and contaminants therein.

As flue gases typically contain sufficient free oxygen and moisture to form sulfuric acid from sulfur dioxide, they may, in principle, be passed over a catalytic bed to oxidize sulfur dioxide therein to the acid. However, for conversion of large portions of the sulfur dioxide at rates which make the process technically feasible, the flue gas must contain a substantial proportion of sulfur dioxide. This limitation renders such a process unsuited for most industrial situations. In addition such systems are quite costly to install and operate.

Catalytic oxidation of the sulfur dioxide content of flue gases after absorption in aqueous scrubbing solutions has also been investigated with such catalysts as iron and manganese sulfates. It has, however, been found that phenolic bodies and other substances present in most flue gases rapidly de-activate these catalysts. Furthermore, rates of oxidation decrease as acid concentration rises. An acidity concentration of about 25 percent is the maximum obtained by such process, with practicality. A concentration of about 75 percent is normally required for sulfuric acid. In addition, the use of an aqueous solution causes a cooling of the flue gases which results in a loss of plume buoyancy.

Therefore, it is a general object of the present invention to provide improved electrochemical oxidization means.

More particularly, it is an object of the invention to provide electrochemical means for oxidizing fluids containing oxidizable materials such as sulfur dioxide, ionized iron, formaldehyde, methanol, sugars and sewage.

Another object of the present invention is to provide means for removing sulfur dioxide from flue gases with economy.

Yet another object of the invention is to provide means for recovering sulfur from the sulfur dioxide content of flue gases in the form of sulfuric acid of marketable concentration.

Another object of the invention is to provide means for recovering sulfur from the sulfur dioxide content of flue gases which means operates at temperatures near those of the flue gases themselves whereby plume buoyancy may be retained.

Still another object of the invention is to provide means for recovering sulfur from the sulfur dioxide content of flue gases in the form of concentrated sulferic acid which means does not require the circulation of a scrubbing solution and which leaves few, if any, particles of fly ash in the acid.

SUMMARY OF THE INVENTION

Briefly described, the present invention is an electrochemical cell comprising a bipolar electrode having two spaced surfaces adapted for exposure to an oxidizing and a reducing agent, respectively. The two electrode surfaces are connected by ion and electron conveyance means.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic illustration of a single cell made in accordance with principles of the present invention.

FIG. 2 is a prospective view of a set of cells such as those shown in FIG. 1 assembled together to form a cell bank.

FIG. 3 is a prospective view of an oxidation system containing a number of cell banks such as those shown in FIG. 2.

FIG. 4 is a cross-sectional view of a fragment of a porous electrode which view shows an orifice of a single electrode pore at one electrode surface.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The electrochemical cell about to be described in more detail functions neither as a classic electrolytic nor galvanic cell. This is due to the fact that it neither requires nor delivers external, electrical energy. Probably its closest analogy in the generally accepted terms of today would be that of a fuel cell inasmuch as chemical oxidization and reduction and electrolysis does occur within the cell itself. But again, the cell produces no exteriorly accessible electrical energy and thus would ordinarily be misdescribed by such terms as "fuel cell", "galvanic cell" or "battery".

In FIG. 1 is shown a single cell made in accordance with principles of the present invention. In general terms the electrochemical cell comprises a porous slab 5, the pores of which contain a liquid electrolyte. Two spaced surfaces 6 and 8 of the slab form a portion of conduits 7 and 9, respectively. With this structure each of the two slab surfaces are exposed to fluids which may pass through one of the conduits. In addition, each surface is in fluid communication with the slab pores whereby the electrolyte within the pores is permitted to flow over the two surfaces, the electrolyte being held thereto by the force of adhesion.

With this structure the solid portion of slab 5 provides a low resistive, electrically conductive path between surfaces 6 and 8 while the electrolyte within the slab pores provides an electrolytic path between the two surfaces.

In operation an oxidizing agent is introduced into conduit 7 and caused to flow over surface 6. At the same time a fluid containing an oxidizable substance is introduced into conduit 9 and caused to flow over surface 8. If the fluids in contact with the two electrodes are of dissimilar electrochemical potential, the oxidizable substance flowing within conduit 9 will become oxidized and the oxidizing agent flowing within conduit 7, reduced. Electrolysis will occur in the electrolyte permitting the flow of ions between surfaces 6 and 8 which now function as cathode and anode, respectively. The porous slab itself will provide a conductive path for the flow of elections between the two electrodes.

With continued reference to FIG. 1 a single electrochemical cell will now be described more specifically. This cell is particularly adapted for use in removing sulfur dioxide from flue

gases and, in the process, oxidizing the sulfur dioxide to sulfuric acid of marketable quality in terms of purity and concentration. In this case porous slab **5** is made of graphitic carbon and saturated with sulfuric acid having a concentration of between 50 percent and 80 percent. Surface **8** is coated with a slurry of polytetrafluorethylene (Teflon) and powdered, activated charcoal for purposes to be hereinafter described. Surface **6**, which functions as a cathode, is also coated with Teflon and powdered, activated charcoal with some areas thereof being left uncoated. Both surfaces are preferably grooved or serrated to provide an increase in surface area for electrochemical reactions. Finally, conduit **7** is connected to an air supply and conduit **9** to a flue.

Flue gases typically contain sulfur dioxide and water vapor while air, of course, contains oxygen. When air is introduced into conduit **7** and flue gases into conduit **9** with the pores and exposed surfaces of graphite slab **5** saturated with sulfuric acid, sulfur dioxide will be oxidized at the anode according to the equation

$$So_2 + 2H_2O \rightarrow SO_4 = + 4H^+ + 2e^- \quad 1.$$

At the cathode oxygen will be reduced to water in accordance with the equation

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad 2.$$

By adding the reactions expressed by these two equations we find the net result of the operation of the cell expressed by the equation

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow SO_4 = + 2H^{115} \quad 3.$$

In this manner sulfuric acid is formed spontaneously and continuously so long as the sulfur dioxide and oxygen are supplied. The electric power generated by the process causes current to flow through the conductive slab between the cell electrodes. Heat developed by the current is conducted from the graphite to the sulfuric acid located within the pores thereof. The heat is then carried from the cell upon emission of sulfuric acid therefrom as subsequently explained. This lost electric power is very small when compared to the rated capacity of a steam-powered electric power plant, for example, by which the flue gases from which sulfur dioxide is to be oxidized are produced. Thus, its loss is well offset by such advantages as the absence of costly, acid-sensitive current collectors and the overall simplicity and economy of the cell as a whole.

During cell operation sulfur dioxide is dissolved in the thin film of sulfuric acid which coats the anode. Upon reaching the electrode surface it is oxidized according to equation (1) forming sulfate ions and liberating hydrogen ions and electrons. The electrons pass through the graphite slab to the cathode where they unite in accordance with equation (2) with oxygen which is absorbed in the film of sulfuric acid thereon. In this process hydrogen ions are consumed, reaching the cathode by diffusion through the electrolytic sulfuric acid contained within the slab, passing from the anode upon which they were formed. This action results in the continuous formation of sulfuric acid at the anode which will tend to absorb water from the flue gases in order to approach equilibrium concentration as governed by the partial pressure of the water vapor contained in the flue gases and the prevailing temperature. As flue gases typically contain 12 –14 percent water vapor and are generally in a temperature range of 250° to 300° F., the resulting concentration will, under such conditions, fall within the range of 65 to 82 percent.

The formation of sulfuric acid on the cell anode will result in a supply of acid excess to that of the needs of the cell itself. As the slab pores are already filled with acid the increase in liquid volume will cause pendant drops to form and fall from those portions of the cathode not coated with the previously-described slurry. This will result in a continuous flow of acid through the porous slab from anode to cathode. The drops of sulfuric acid fall into collection troughs (not shown) for accumulation, storage and subsequent shipment. As the sulfuric acid is collected from the cathodic side of the electrode it is free of fly ash since it has, in effect, been filtered in passing through the porous slab.

FIG. **2** illustrates a cell bank **11** comprising four porous, conductive slabs **5** saturated with sulfuric acid and coated in the manner described in the discussion of FIG. **1**. The slabs are stacked in spaced, parallel relation to provide conduits therebetween. Each is separated from the next by means of a spacer **17** which may be of the same material as that of the slabs themselves. As seen in the figure, the conduits extend through the cell bank in horizontal and vertical directions, alternatively. When air is passed vertically and flue gases horizontally through the bank, as indicated by the arrows and legend, the cell bank oxidizes sulfur dioxide in the flue gas to sulfuric acid as hereinabove explained. A number of such cell banks may in turn be assembled to form an oxidation system such as that shown in FIG. **3**.

Located atop each flue gas passage is a spray pipe **10** providing means whereby each passage may be periodically sprayed with water or an air blast to dislodge deposits of fly ash. After the elapse of a substantial period of operation it may become necessary to brush out the reaction passages to dislodge deposits not washed off by the periodic sprays. However, since adhesion of solid particles to Teflon-coated surfaces is very weak, the need for such brushing is quite infrequent.

As previously mentioned, most areas of the porous slab surfaces are coated with a mixture comprising Teflon. The purpose of this is to treat the surfaces with a hydrophobic substance to prevent the pore orifices from becoming flooded which condition would block access of diffusing gas and eliminate the super-meniscus. The "super-meniscus" is a phenomenon associated with porous electrodes. It is described in Journal of the Electrochemical Society 110 (1963) at pages 145 and 152, in Advances in Energy Conversion 4 (1964) at page 109, and in Journal of the Electrochemical Society 112 (1965) at page 1166. It should be appreciated that these slab surfaces form gas-diffusion type electrodes upon which sulfur dioxide diffuses in its gaseous state into the slab pores where it meets the meniscus of the electrolytic sulfuric acid along the walls of the pores. Electrochemical reaction is believed to occur at these sites. This action may be more clearly understood by reference to FIG. **4** in which sulfur dioxide exists as dissolved molecules in the thin coat of sulfuric acid overlaying anode **8**. Arrows **15** indicate the passage of the sulfur dioxide into super-meniscus region **12** of pore **16** in transit to meniscus **13**. Electrochemical reaction is believed to occur in the super-meniscus within a distance of some millimeters from intrinsic meniscus **13**.

In addition to a hydrophobic substance the electrodes are also coated with a catalytic agent to enhance the electrochemical reactions and to produce a high current density. Activated charcoal is an effective catalyst in oxidizing sulfur dioxide although platinum, which is even more effective, could be used with reasonable economy in small quantities such as 1 to 3 mg./cm.^{2} provided that reduction of sulfur dioxide to sulfides or other catalyst poisons is avoided.

With concentrated sulfuric acid as the electrolyte, temperatures as high as 350° F. may be sustained. The cooling effect of air circulated over the cathode need not be great since the stoichiometric demand for air is only 1/133 that of the volume of the flue gases. Furthermore, heat developed by the flow of current within the bipolar electrodes, and by dilution of the acid produced with water absorbed from the flue gases, will tend to make up any heat losses. Consequently, the system typically operates at between 300° and 350° F. which largely preserves plume buoyancy.

Because the catalytic oxidation of sulfur dioxide in the presence of iron or manganese salts is inhibited by the presence of phenols, the system has been tested with phenol added to the electrolyte. After a brief period of slight increase the current has been found to return to normal thereby indicating that phenol does not seriously interfere with the electrochemical oxidation of sulfur dioxide in utilizing this cell.

Furthermore, it has been found that other electrolytes, such as 10 percent phosphoric acid, may be substituted for sulfuric acid within the pores electrode in producing sulfuric acid. In time it will, of course, be expended from the system.

It should be understood that the described embodiments are merely illustrative of applications of the principles of the invention. Obviously, many modifications and substitutions may be made in these specific configurations and materials without departing from the spirit and scope of the invention as set forth in the following claims.

What is claimed is:

1. Apparatus for removing sulphur dioxide from flue gases by converting it to sulphuric acid without any electrical power requirements, comprising:

a porous body with large first and second opposing surfaces,

said first surface functioning as an anode and said second surface functioning as a cathode;

said body providing a continuous internal low resistance short circuiting electrical conducting path between said first and second surfaces;

said body having a multiplicity of continuous small passageways therethrough extending uninterruptedly from said first surface to said second surface and opening at both of said surfaces,

said passageways adapted to be filled with a liquid electrolyte (comprising aqueous sulphuric acid) providing continuous electrolyte paths between said first and second surfaces,

said electrolyte being exposed at both of said surfaces,

first conduit means communicating with said first surface for applying sulphur dioxide containing flue gasses directly against said first surface, and

second conduit means communicating with said second surface for applying air directly against said second surface,

said first and second conduit means providing for removal of sulphuric acid from said porous body,

whereby sulphur dioxide is removed from said flue gasses by direct electrochemical conversion to sulphuric acid at said body.

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