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BURNING PROCESS FOR RECOVERING SULFUR FROM THE EARTH

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This invention relates to an improved process and apparatus for recovering sulfur from the earth.

As is well known, there are numerous deposits of sulfur at various points in the earth, which are actually relatively rich in these substances, but which are in some way so positioned in the earth, or so mixed with other materials, as to render it impossible to mine these deposits by conventional methods. For instance, there are bodies of sulfur ore in the earth in which the sulfur is so interspersed with gangue as to effectively prevent recovery of the sulfur by the usual Frasch process. These ores are normally porous, and may typically contain between about 15% and 30% sulfur. In the past, various proposals have been made for processes to recover the sulfur from such an ore body, but I know of none which has proven successful.

The general object of the present invention is to provide a process which is capable of recovering from the earth the above discussed substance which heretofore could not be mined effectively. As will appear, the present process and apparatus may be utilized with a minimum of expense, to bring the sulfur to the surface of the earth, in a form essentially free of other substances. Also, if desired, in the case of sulfur recovery, some or all of the sulfur may be recovered in the form of sulfur dioxide gas, which may then either be stored as a gas or liquid or used in the manufacture of sulfuric acid.

In performing the process of the invention, the sulfur is converted to a condition in which it is easily recoverable from a location deep within the earth, with the conversion being effected very uniquely by actually burning a portion of the sulfur or other substance in situ in the earth. This burning of some of the substance itself produces heat in the earth which acts to melt additional portions of the surrounding sulfur, so that this material may then be easily withdrawn upwardly to the surface of the earth in molten free-flowing condition. In the simplest variation of the invention, the molten material is pumped upwardly by the pressure of the gases of combustion produced by the burning operation itself. In instances in which it is desired to produce sulfur dioxide from the ore, all or most of the sulfur may be burned in situ, and the resulting sulfur dioxide may then be brought to the surface of the earth in gaseous form.

The above and other features and objects of the present invention will be better understood from the following detailed description of the typical embodiments illustrated in the accompanying drawing in which:

FIG. 1 is a vertical section through a first type of apparatus for recovering an earth substance in molten form;

FIG. 2 is a view similar to FIG. 1, but showing an arrangement in which the pumping and combustion supporting apparatus is somewhat more complex than in FIG. 1;

FIG. 3 shows apparatus especially adapted for the recovery of sulfur from the earth, partially in the form of molten sulfur and partially in the form of sulfur dioxide and ultimately sulfuric acid; and

FIG. 4 shows still another form of the invention.

In FIG. 1, I have represented at 10 an ore body or layer of material spaced beneath the surface 11 of the earth, and containing a substance to be recovered. This body 10 may typically consist of a porous intermixture

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of sulfur and siliceous or other gangue materials. Above the ore body 10, there is illustrated in FIG. 1 an overburden or upper stratum 12. This layer 12 may in most instances be formed of a material or materials having a melting temperature well above the melting temperature of the substance to be recovered from layer 10.

In recovering the material from ore body 10 by the apparatus of FIG. 1, the first step is to drill into the earth a hole or bore 13, which may initially be of a uniform diameter through the entire vertical distance from the surface of the earth 11 down to the bottom 14 of the hole. In FIG. 1, the lower portion of this bore as originally drilled is represented in broken lines at 15. After bore 13 has been drilled into the earth, there are installed in this bore two desirably concentric pipes 16 and 17, with the former being disposed about the latter to provide an annular vertically extending passage 18 between the pipes. As will be understood, each of these pipes 16 and 17 will in most cases be formed of a series of separate sections or stands, threadedly joined together in an end-to-end series to form overall pipe assemblies of proper lengths to reach the producing formation. The inner pipe 17 extends downwardly to a location 19 spaced but a short distance above the bottom 14 of the bore. The outer pipe 16, on the other hand, terminates at a point 20, spaced well above the lower end 19 of pipe 17. The upper end of annular passage 18 about pipe 17 is suitably sealed or closed by conventional well head apparatus of any desirable type, as represented by the seal diagrammatically represented at 21 in FIG. 1. A gas containing oxygen is fed into the upper end of annular space 18 through a fitting represented at 22, and from a source of such gas under pressure indicated at 23. This gas coming from source 23 may in some instances be pure oxygen, and in other instances be air or another mixture of gases containing oxygen and capable of supporting combustion. Source 23 preferably maintains a continuous flow of such combustion supporting gas downwardly through passage 18, to emit continuously from the lower end 20 of pipe 16. This rate of oxygen feed to the production zone may be great enough to support combustion of the sulfur in body 10 continuously. Molten production fluid flows upwardly through inner pipe 17 and discharges from the upper end of that pipe through a line 24 leading to an accumulation tank 25.

In conjunction with the apparatus thus far described, there is also provided some means for initiating combustion of the production substance near the lower end of pipe 16. This means for starting the combustion may be simply a mass of burning thermite or other material injected into the upper end of annular space 18 to fall downwardly therethrough to the production zone, or may be any other convenient type of igniting system. In FIG. 1, I have typically represented an arrangement in which there is provided about inner pipe 17 at a location directly below the lower end 20 of pipe 16, an annular mass 26 of highly combustible material, typically thermite, which is ignited electrically by current fed to body 26 through wires 27 extending upwardly to the surface of the earth. These wires connect at the surface of the earth to a power source 28, through a switch 29 whose closure fires the combustible charge 26.

Assuming that the bore 13 has been drilled downwardly to location 14 (with the bore being of a uniform diameter for its entire length), and assuming that all of the apparatus illustrated in FIG. 1 is in position as shown, the first step in placing the apparatus in operation may be to actuate the air or oxygen source 23 to commence a flow of air or oxygen downwardly through passage 18, and then upwardly through pipe 17 and to tank 25. This tank 25 may have an upper vent 30, through which air or gases of combustion in the upper portion of the tank

may escape to the atmosphere, leaving any production liquid which comes upwardly through pipe 17 in the tank. After the air or oxygen flow has been commenced, the operator closes switch 29 to fire combustible charge 26. This charge is designed to raise the temperature of the portion of ore body 10 which is disposed directly adjacent the lower end of pipe 16 to a value causing the combustible sulfur to burn. The rate of oxygen delivery through passage 18 is maintained at a value such as to continue this burning even after charge 26 is gone, and as long as it is desired to continue the production of sulfur or the like from zone 10. The heat of combustion is high enough to melt a large amount of the sulfur forming the wall of bore 13, so that this molten material falls downwardly to the bottom of bore 13, as represented at 31. The burning action progressively enlarges the lower portion of the bore to form a cavity 32 considerably larger in diameter than the upper portion of bore 13. Preferably, most of the burning takes place in the upper portion of cavity 32.

The molten material 31 which falls to the bottom of the cavity is forced upwardly through pipe 17 by the pressure of the gases of combustion resulting from the burning operation. This molten material flows into tank 25, and any air and other gases mixed with the molten material is vented off to the atmosphere through vent 30. If the pumping action reaches a point where all of the liquid 31 has been removed from the bottom of the cavity, then the gases of combustion flow upwardly through pipe 17 and to the atmosphere without intermixed liquid until additional molten material accumulates in the bottom of the cavity, at which time the liquid pumping action recommences automatically. It is also noted that the presence of upper stratum 12 above lower ore body 10 effectively prevents the upward advancement of the burning or melting action beyond the interface 33 between the two strata, since it is assumed that layer 12 is not readily combustible or meltable.

There may be provided in the line leading from oxygen or air source 23 to passage 18 a variable passage throttle valve 34, which is capable of regulating the rate of air or oxygen delivery, and thereby varying the temperature maintained in the cavity 32. This temperature is maintained at a value sufficiently above the melting temperature of the substance being produced to assure arrival of the substance in molten readily flowable condition in tank 25. For this purpose, the temperature may be regulated either by reference to a reading produced at the surface of the earth by a temperature responsive element located within cavity 32, or by merely noting the condition of the produced substance as it reaches tank 25.

In recovering sulfur by the present process, an additional problem arises, in that sulfur has the peculiar tendency to become more viscous in its molten state if overheated beyond a certain critical temperature (320° F.). Since the ignition temperature of sulfur (510° F.) is well above this critical 320° F. temperature, the burning of the sulfur must be either relatively slow and localized at the upper end of cavity 32, or else intermittent, in order that the molten sulfur at the bottom of cavity 32 may be sufficiently mobile to allow it to be elevated to the surface of the earth. This result may be attained by admitting air or oxygen to the burning zone only very slowly, or by first burning for a short period at a relative high temperature, and then discontinuing the heating for a period sufficient to allow the sulfur to cool to a temperature at which it again becomes mobile, so that the liquid sulfur may flow to the surface of the earth. Such intermittent burning may be effected by injecting burning thermite into the air stream from source 23 to commence each burning cycle, with the burning thermite being carried downwardly to the lower end 20 of the pipe 16, and there serving to ignite the combustible ore substance. Between burning periods,

the air flow may be shut off, to extinguish the flame in cavity 32.

FIG. 2 represents an arrangement which is basically very similar to that of FIG. 1, but in which there are four preferably concentric spaced pipes 35, 36, 37 and 38 extending downwardly from the surface of the earth to the burning zone. These pipes form four concentric passages 39, 40, 41, and 42. The inner two pipes 35 and 36, and the passages therein, extend downwardly to a location very near the bottom of the initial bore 43 formed in the earth. The outer two pipes and their passages terminate at a location spaced well above the lower end of the bore. Air or oxygen for supporting combustion of the earth substance adjacent the lower ends of outer pipes 37 and 38 may be fed into the upper end of passage 41 from a source represented at 44, with the combustion being commenced in any suitable manner, as by an electrically ignited highly combustible charge 45 corresponding to charge 26 of FIG. 1. The gases of combustion produced by burning within cavity 46 may be discharged upwardly from the cavity through outer passage 42 leading to a vent line 47 communicating with the atmosphere.

The molten sulfur is pumped upwardly to the surface of the earth through passage 40 disposed between the two inner pipes 35 and 36, and flows from the upper end of that passage into an accumulation tank or chamber represented at 48. In the FIG. 2 arrangement, this upward flow of the molten production liquid is effected by means of an air-lift type of pumping system, consisting of a blower 49 at the surface of the earth acting to produce a rapid flow of air downwardly through inner passage 39, and upwardly through passage 40, to entrain and carry with it the molten liquid. For causing a reversal of air flow at the bottom of this air-lift system, there may be provided any suitable type of deflector, typically represented at 50, acting to direct the air from inner passage 39 upwardly through outer passage 40, at a location to cause the desired upward pumping of the molten fluid. Since air-lift systems in general are well known, no attempt has been made to illustrate the deflector 50 in any detail.

In placing the FIG. 2 apparatus in operation, the flow of air downwardly through passage 41 may first be commenced, following which charge 45 or its equivalent is ignited to commence combustion of the sulfur along the bore wall adjacent charge 45. The air-lift system is then placed in operation to pump upwardly molten sulfur as it accumulates at 51 at the bottom of cavity 46.

FIG. 3 illustrates an arrangement which is considered most desirable for use in producing sulfur and sulfur dioxide from a porous ore body 58 located beneath an overburden or upper stratum 59. In FIG. 4 there are drilled three or more bores 60, 61 and 62, extending downwardly to different locations in the ore body 58. Bore 61 extends downwardly to a location 63 spaced beneath the lower ends 64 and 65 of the other two bores. Also, the two bores 60 and 62 may be located at opposite sides of main bore 61, as shown. A single pipe 66 typically extends downwardly within bore 62 to the location 64, and conducts oxygen from a pressurized source 67 to zone 64. The burning of the sulfur is initiated, and takes place, primarily at the lower end of pipe 66, being initiated in any suitable manner, as by injection of burning thermite into the oxygen stream, or by electrically igniting a highly combustible charge 68 lowered into the pipe on a wire line. The cavity at zone 64 is initially of the same diameter as the rest of bore 62, but becomes enlarged as a result of the burning action.

The heating of the sulfur in ore body 58 by the burning at zone 64 melts much of the sulfur in the ore body, causing that sulfur to flow downwardly through the porous ore, and to the level of the recovery well or zone designated 63. From this well, the molten sulfur is pumped upwardly to the surface of the earth and into an accumu-

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lation tank or chamber 164 through the annular passage between two pipes 165 and 166. Such elevation of the molten fluid may be effected by means of an air-lift, to which pressurized air is supplied from a source represented at 167, which directs the air downwardly through inner pipe 165. A suitable deflector represented at 168 reverses the direction of air flow at the bottom of the well, to direct the air upwardly through the outer annular passage between pipes 165 and 166, with this air flow entraining and carrying with it the molten sulfur.

The combustion at zone 64 produces substantial amounts of sulfur dioxide, which gas is able to flow through the porous ore body 58 and into a cavity 65 formed at the lower end of bore 60. From this cavity, the sulfur dioxide flows upwardly through a pipe 69, to a unit 70 which oxidizes the sulfur dioxide to sulfur trioxide. The sulfur trioxide is then converted to sulfuric acid by conventional equipment represented at 71, and emits from that equipment at 72 in the form of sulfuric acid. If desired, the units 70 and 71 may of course be omitted, with the sulfur dioxide being stored directly in the form of a gas or liquid rather than being converted to an acid.

In order to regulate the rate of combustion of the sulfur at zone 64, I may mix with the oxygen from source 67 varying amounts of sulfur dioxide from delivery pipe 69. For this purpose, a recirculating line 73 is provided, through which sulfur dioxide is delivered under pressure by a pump 74 into the upper end of pipe 66. A mixing valve 75 may be provided at the juncture of the oxygen and sulfur dioxide lines, for regulating the ratio of sulfur dioxide to oxygen. Also of course suitable valves may be provided for completely closing off all flow of sulfur dioxide and oxygen into the ore when desired.

The heat produced by the burning at 64 may be regulated to maintain a maximum overall rate of production of molten sulfur into tank 164. These temperatures should be so controlled that the sulfur does not cool to a temperature at which it will solidify, and further should be so controlled that the sulfur is not elevated in temperature for too long a period, or over too wide an area, to temperatures at which the sulfur becomes more viscous, and slows the rate of sulfur flow into recovery well 63 for that reason. In the preferred operational process, the burning at zone 64 is continued until the effect of the heating is great enough to raise the temperature at zone 63 to the melting temperature of sulfur, or more desirably until the temperature at 63 reaches about 315° F. At that time, the combustion at zone 64 may be halted or throttled back, so that the general temperature of the ore body above zone 63 declines, through heat diffusion. The molten but viscous sulfur in the hotter region above will then progressively revert to a mobile condition and drain into the recovery well at 63. It will of course be understood that the apparatus of FIG. 4 may be utilized, if desired, to recover only the molten sulfur, or to recover only the sulfur dioxide.

FIG. 4 shows still another form of the invention, which may be considered the same as that of FIG. 1, except that there is purposely provided about the outer pipe 76 a generally annular space 77 through which some of the gases of combustion are purposely allowed to escape upwardly. This arrangement may be utilized where the combustion at the production zone acts to develop an excessive quantity of the gases of combustion, or perhaps where it is desired to vent off all of the gases of combus-

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tion and utilize other means for pumping the production fluid upwardly through inner pipe 78. As in the first form of the invention, the produced sulfur accumulates within a chamber or tank 79, while the oxygen or air for maintaining combustion at the burning zone is supplied by a source represented at 80.

Two major advantages of the above discussed processes over the conventional Frasch process for recovering sulfur reside in, first, the utilization of the in situ sulfur as the only required fuel for the melting of the remaining sulfur, and second, the elimination of the necessity for large supplies of water for recovering the sulfur. As will be apparent, both of these advantages are of great moment in areas not well supplied with fuel and water.

I claim:

1. The process of recovering sulfur from the earth comprising burning some of said sulfur in situ beneath the surface of the earth and at a temperature well above the critical temperature of 320° F. at which the sulfur increases in viscosity, melting additional portions of said sulfur by the heat of said burning to a temperature above said 320° F. critical temperature with the result that said additional portions after melting become highly viscous, interrupting said burning for an interval sufficient to allow some of the viscous melted sulfur above said critical temperature to cool to a temperature less than 320° F. but with the sulfur still in melted form and therefore at a viscosity lower than before said cooling, recovering said sulfur which has decreased in temperature while it is melted but cooler than said critical temperature, and repeating said steps of burning some of the sulfur, thereby heating additional sulfur to high temperature, interrupting the burning, and then cooling the sulfur to a low viscosity form, through numerous successive intermittent cycles, so that additional quantities of sulfur may be recovered.

2. The process of recovering sulfur from a cavity in a sulfur containing formation in the earth, comprising burning some of said sulfur in situ in an upper portion of said cavity and at a high temperature well above the critical temperature of 320° F. at which the sulfur increases in viscosity, melting additional portions of said sulfur by the heat of said burning to a temperature above said 320° F. critical temperature with the result that said additional portions after melting become highly viscous, interrupting said burning for an interval sufficient to allow some of the viscous melted sulfur above said critical temperature to cool to a temperature less than 320° F. but with the sulfur still in melted form and therefore at a viscosity lower than before said cooling, whereby the melted sulfur may flow downwardly to the bottom of said cavity, recovering said melted sulfur from the bottom of the cavity while it is melted but cooler than said critical temperature, and repeating said steps of burning some of the sulfur in said upper portion of the cavity, thereby heating additional sulfur to high temperature, interrupting the burning, and then cooling the sulfur to a low viscosity form, through numerous successive intermittent cycles, so that additional quantities of sulfur may be recovered from the bottom of the cavity.

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