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3,410,604

IN-SITU OXIDATION REACTION WITHIN A SUB-SURFACE FORMATION CONTAINING SULFUR

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This invention relates to production of sulfur or sulfur compounds from underground sulfur bearing formations. More particularly, this invention relates to carrying out an in-situ oxidation reaction wherein sulfur and/or compounds are produced.

Various techniques have been proposed for the recovery of sulfur from underground formations and for the treatment of sulfur bearing formations. For the recovery of sulfur from sulfur producing formations operations which involve hot water injection or steam injection into at least one well have been proposed.

In accordance with the in-situ oxidation reaction method of this invention, a high temperature zone is established in the formation in the vicinity of a well bore by suitable heating means. The heating means may comprise an electrical heating device or a gas fired bottom hole igniter or heater. A suitable device for initiating in-situ combustion within a bore hole is described in U.S. 2,997,105 or U.S. 2,771,140.

Upon introducing an oxygen-containing substance, such as air, into the thus-heated producing formation via the injection well bore, a high temperature zone (temperatures in the range of 500° F.-2,800° F., usually in the range of 625° F.-1,800° F.) is created by the reaction between oxygen and the sulfur bearing material within the formation. This high temperature zone will move outwardly into the formation from the well bore, in the direction of flow of the hot gaseous reaction products.

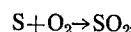
Leaving the high temperature reaction zone is a relatively high temperature gas stream at substantially the same temperature which, as it moves outwardly into the formation, loses heat to the formation. By this method the high temperature reaction zone moves in a more or less radial manner outwardly from the well bore without further direct application of heat to the area immediately surrounding the well bore. The distance the high temperature reaction zone moves outwardly, and accordingly the volume of the producing formation swept by or located within the high temperature in-situ oxidation reaction zone, is determined by the relative magnitudes of the rate of heat generation (combustion of combustible material), the heat capacity of the formation, the rate of heat loss to the surrounding formation, and the total amount of reactable material present.

The following mechanisms are considered to be important in an underground in-situ oxidation reaction operation for the movement of the high temperature zone radially outwardly from the well bore into the sulfur bearing formation. As the high temperature reaction zone approaches a given volume of the sulfur-containing formation, the temperature of this volume of formation rises. This results in the liquefaction of the sulfur or sulfur compounds. These fluids may then be moved under the influence of the hot gas stream continuously emanating from the high temperature reaction zone. As the temperature of this volume of formation continues to rise distillations of the liquids therein begin. The products of these distillations condense in cooler regions of the formation removed from the high temperature combustion zone in the direction of gas flow. As the temperature

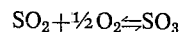
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continues to rise and the oxygen content of the incoming gas to the given volume of formation increases due to depletion of combustible compounds in preceding regions or volumes of the formation, a point will be reached at which the combustible material will begin to chemically combine with the oxygen with the resulting release of heat to the formation and the gas stream emanating therefrom. The type reaction will depend on the chemical composition of the sulfur bearing compounds present and also on combustible materials other than sulfur that are present.

One general reaction, given by way of example and not by way of limitation, is the reaction between sulfur and oxygen:



If the oxygen utilization is not complete another type reaction would be



The heat released by these reactions is carried away by the onmoving gas stream and also by conduction to the adjacent regions of the formation. This heat is sufficient to melt additional sulfur above and below the high temperature reaction zone and allow sulfur in those portions of the reservoir to migrate outward in the direction of gas flow and/or downward into the high temperature reaction zone depending on the vertical and horizontal permeability. When the available combustible materials have been burned away there remains a volume of substantially sulfur free formation in the volume thus treated which, unless otherwise treated, is then gradually cooled by the relatively cool combustion supporting gas or air entering the thus-treated given portion of the formation via the well bore.

From the above-indicated considerations, it is clear that the rate of heat energy released within the formation is a function of the quantity of fuel or reactable materials present therein, which is dependent upon type and quantity of the reactable material originally in place and/or combustible material entering into the various chemical reactions. The rate of heat release is also dependent upon the rate at which oxygen is supplied to the reaction zone or, in other words, the rate at which the exothermic combustion process within the formation undergoing treatment is effected. The rate at which heat can be transferred ahead of the high temperature reaction zone should be dependent on the rate at which the gaseous products of combustion leave the high temperature reaction zone and should be to some extent dependent upon conduction through the formation itself. Accordingly, control of the in-situ oxidation reaction is exercised by controlling the oxidation or combustion occurring in the process, such as by controlling the amount of oxygen or other oxidizing agent introduced into or present within the high temperature reaction zone in contact with the reactable residues therein. The chemical reactions are controlled in a number of ways. For example, chemical reactions can be controlled by altering the pressure and temperature. The pressure is established over a relatively large range by increasing or decreasing the oxidant injection pressure at the input well, to result in the desired chemical reaction. Also the temperature at the reaction zone is variable over a relatively large range by changing the composition as well as the rate of injection of the oxidizing agent. Either pure oxygen or air with inert gases added may achieve the desired composition of oxidizing gas.

Accordingly, it is the object of this invention to provide an improved method for the treatment of sulfur containing formations to enhance or otherwise improve the recovery of sulfur and/or sulfur compounds therefrom by an operation involving an in-situ oxidation reaction.

It is another object of this invention to provide a method of recovering sulfur or sulfur compounds from one or more producing wells that surround an injection well. In a forward oxidation operation, an oxidizing agent is introduced into an injection well and the high temperature reaction zone, gases, and liquids move in the same direction to the producing well or wells.

In a reverse oxidation embodiment, a high temperature zone is established in one or more producing wells and air or suitable oxidizing agents are introduced through an injection well or wells located some distance away. The high temperature reaction zone then moves away from the producing well toward the injection well. The sulfur or sulfur compounds are produced at the production well.

In another embodiment high temperature zones are initiated in both the injection and production wells at the same time in order to increase the oxygen utilization of the process.

How these and other objects of this invention are accomplished will become apparent with reference to the accompanying disclosure. In at least one embodiment of the practice of this invention, at least one of the foregoing objects will be achieved.

The practice of this invention is particularly applicable to an in-situ oxidation reaction operation employing a plurality of wells, that is, at least one injection well and at least one production well. The total oxygen or heat requirement of the in-situ oxidation reaction operation may be supplied by introducing into the formation undergoing treatment a material or compound which reacts with the formation fluids, particularly water, to yield elemental oxygen or a thermally unstable compound which decomposes at the temperature at which the in-situ oxidation reaction is to be carried out, or at a lower temperature, to yield oxygen. Desirably an in-situ oxidation reaction operation carried out in accordance with the practice of this invention utilizes extraneously introduced via the well bore elemental oxygen, either substantially pure oxygen, air, or air enriched with respect to oxygen or having a reduced oxygen content such as an oxygen content in the range 6.1-80 percent by volume.

In one embodiment of the practice of this invention a high temperature zone is established in the vicinity of the injection well bore. A combustion supporting or an oxygen bearing gas, such as air, is introduced continuously or intermittently into this heated injection well bore. A high temperature reaction zone moves out radially from the injection well toward the production wells. At the production wells there will be produced either sulfur dioxide, sulfur trioxide, hydrogen sulfide, sulfur vapors and inert gases injected along with the oxidizing agent, such as nitrogen and argon that enter with the air. The produced compounds will appear individually or as a mixture of one or more of the named vapors and gases along with other possible products of the reaction depending on the nearness of the reaction zone to the producing well and the type of formation being treated. Also, liquid sulfur may be displaced to the production well along with the hot combustion gases when the formation in the vicinity of the producing well is above the melting point of sulfur.

In another embodiment of the invention water or other suitable heat scavenging materials can be injected into the hot formation behind the reaction zone in order to move additional sulfur to the producing well. This water or other heat scavenging material will be injected simultaneously with the air so as to move the heat stored in the depleted section of the reservoir ahead of the

burning front but so as to not quench the high temperature reaction or burning front. Alternatively, the heat scavenging material will be injected as a large slug after the burning and air injection phase of the operation is complete. Intermittent slugs may be injected followed by an air injection period.

In another embodiment of this invention where the formation characteristics do not permit the continuous injection of air due to lack of effective permeability to gas, either due to rock or sulfur properties, the following process will be followed: Prior to initiation of the burning front a fracture system (either horizontal, vertical or combination of these) is established in the formation between the wells, for example, by any of the well known hydraulic fracturing techniques. When a permeability to gas exists between the wells, the formation is ignited and the process proceeds in the manner described above.

In still another embodiment of the invention a high temperature zone is established in each of the producing wells. Oxidizing material is then injected into the injection well or wells to establish a reaction zone in the heated area. The burning reaction zone then moves in a countercurrent manner to the injected oxidizing material, in a direction toward the injection well. The gases and vapors produced by the chemical reaction and distillation that takes place at the reaction zone then pass through the depleted hot volume and are produced, along with any inerts, as gases, vapors and liquids from the producing wells.

As described above, where a natural effective permeability to gas does not exist in the formation, a fracture system can be created and the reverse burn can then be operated.

A more detailed description of how the process operates in a given type of reservoir is now presented to show how the operation would proceed under these geological conditions. Much of the elemental sulfur of the world is obtained from the sulfur-bearing porous limestones in the salt-dome cap rocks of Texas and Louisiana, where it is common to find an anhydrite formation on top of the rock salt formation. The calcite formation lies on the anhydrite with the lower portion being sulfur bearing and the upper portion being a calcite cap rock. Various formations and unconsolidated sediments may be found between the earth's surface and the calcite cap rock. Injection wells and production wells of this invention are completed in such a manner as to insure that the injected oxidizing gas enters the sulfur bearing portion of the calcite formation and the produced sulfur oxides enter the well bore in the sulfur bearing strata of the reservoir.

An oxidizing agent is injected into and through the sulfur bearing formation if sufficient permeability exists. Where sufficient permeability to gas does not exist in the native condition, a fracture system is created by hydraulic means. After sufficient permeability to gas had been established in the formation between the injection and production wells, a high temperature zone, approximately 1,000° F., is established in the injection well by use of burners or heaters. An external heat source operates in the well bore until an exothermic oxidation reaction had been initiated in the formation as evidenced by the production of sulfur oxides in the produced gas. The heater or burner is then removed and the operation continues with the oxidation reaction in the formation now supplying the continuous heat source necessary for a sustained operation.

A high temperature heat source results in the melting of sulfur in and ahead of the reaction zone. Amorphous sulfur melts at 248° F., monoclinic sulfur melts at 246° F., and rhombic sulfur melts at 235° F. Thus, when the temperature of the formation increases into the temperature range of 235° F. to 250° F. the sulfur will melt and become mobile. This mobile sulfur tends to flow or migrate into the flow channels through which the injected gas is flowing. Eventually liquid sulfur will contact formation that is below the melting point of sulfur and upon

cooling will start to return to the solid state. This, of course, would tend to block off the flow channels through which the gases are flowing.

Sulfur has an unusual viscosity-temperature relation in that the minimum viscosity is encountered at about 230° F. where the viscosity is about 12 centipoises. The viscosity increases rapidly with temperature and reaches a maximum value of about 56,000 centipoises in the temperature range of 350° F. to 370° F. The viscosity then decreases with increasing temperature till a viscosity of about 80 centipoises exists near its boiling point of 830° F. Thus, while there is a wide range in the viscosity of liquid sulfur, it is mobile in the liquid state between 235° F. and 833° F.

The reduction in effective permeability to gas that will result from the solidification of sulfur in the flow channels will be reflected by an increased pressure requirement on the surface injection system in order to maintain a constant rate of air injection. At this point, it is desired to force the molten sulfur back into the high temperature reaction zone in order to maintain air injectivity and continued high temperature oxidation of the sulfur. According to the method of this invention, this is accomplished in either of two ways: The injection well will be back-flowed to create a pressure sink at that point. This will cause the molten sulfur to reverse its direction of flow and the passage of gas through the molten sulfur that is approaching its solidification temperature will result in the reestablishment of the gas flow channels. When sufficient permeability to gas has been reestablished, the injection of air is resumed in the normal manner. A second method will be to stop injection of air into the regular injection wells and inject air into the production wells to accomplish the same results as achieved by back-flowing the injection wells. The method chosen will depend on the severity of the blockage, location of the high temperature reaction zone relative to the injection and producing wells, analysis of the gases being produced at that time, and conditions of pressure and temperature being maintained.

By careful manipulation of the injection system, a continuous generation of sulfur oxides is maintained during this phase of the development.

Conduction of heat vertically upward from the high temperature reaction zone will result in migration of the sulfur in the upper portion of the sulfur bearing formation down into the high temperature reaction zone if vertical permeability exists. This will result in a high vertical sweep efficiency and better recovery of the sulfur. In time, however, this migration of sulfur down into the reaction zone will result in a permeability to gas being created between the injection point and the calcite cap rock. In certain cases this will result in migration of the injected air through the unsaturated or barren portion of the reservoir rather than through the sulfur bearing portion of the formation. If this occurs there can be a serious loss in oxygen utilization. Thus, a method of minimizing this loss in oxygen utilization is provided.

The primary object of the invention is to produce sulfur oxides to be recovered and processed. The unreacted oxygen that is being produced at the production well will reach a concentration that is sufficient to sustain a continuous high temperature reaction zone in the vicinity of the production well. At the same time a like concentration will exist between the injection well and the production wells. Thus, an external heat source is operated in the producing well for a short period of time to establish a high temperature reaction zone in that vicinity.

That portion of the unreacted oxygen that by-passes the original high temperature reaction zone or that passes through the zone unreacted, now must pass through a second high temperature zone prior to being produced. With the existing pressure gradient being toward the producing well, migration of sulfur will be in that direction assuring a pool of molten sulfur for the unreacted oxygen

to pass through. This describes operations where the reservoir characteristics dictate that both the forward oxidation reaction method and the reverse oxidation reaction method be used in order to efficiently produce the sulfur oxides. Under other reservoir conditions either the forward method or the reverse method may operate efficiently without having both in operation simultaneously.

It is evident that after prolonged operation in a given pattern there will exist in the region between the high temperature oxidation zone and the producing well reservoir temperatures sufficiently high to maintain the sulfur in that region in a molten state. At that point it will be possible to produce a significant amount of elemental sulfur along with the sulfur oxides from the production wells.

In summary, this invention discloses a method or methods of producing sulfur or sulfur compounds by either a forward or reverse in-situ oxidation reaction. Fracturing allows air injection and water injection to scavenge the heat stored in the depleted volume of the reservoir and are employed in certain aspects of the invention.

Having described the invention in connection with certain specific embodiments thereof, it is to be understood that further modifications may now suggest themselves to those skilled in the art and it is intended to cover such modifications as fall within the scope of the appended claims.

What is claimed is:

1. A method of producing sulfur from a sub-surface formation where at least two spaced apart wells penetrate a sulfur bearing formation which comprises:

- (a) establishing in the region of at least a first of said wells a high temperature zone of the order of 1,000° F.,
- (b) introducing a flow of combustion supporting agent into one of said wells to sustain combustion reactions of said sulfur to form gaseous sulfur compounds, and
- (c) producing said compounds through a second of said wells in gaseous form.

2. A method of claim 1 wherein ignition is accomplished in the sulfur bearing formation in the vicinity of said second well whereby an oxidizing agent injected into said first well moves from said first well to said second well to utilize said agent by passing through the high temperature zone adjacent to said second well and thus moving the high temperature reaction zone in a counter-current manner toward said first well for production of the sulfur or sulfur compounds from said second well.

3. The method of claim 1 wherein a reservoir with insufficient native permeability to gas is fractured before oxidation is initiated.

4. The method of claim 1 further comprising injecting water into one of said wells of step (b) to scavenge heat from behind the reaction zone and move it ahead into the cold or cooler volume of the reservoir.

5. The method of claim 1 wherein high oxygen utilization is maintained when by-passing of the high temperature reaction zone by said combustion supporting agent occurs, whereby a second high temperature zone is initiated at the producing well to utilize this unreacted oxygen, and thereafter two high temperature reaction zones are maintained in that well pattern.

6. The method of claim 1 wherein permeability to the injected gas is maintained when liquid sulfur which starts to solidify in the flow channels ahead of the high temperature reaction zone by reversing the pressure gradient by injection into the producing well on an intermittent basis to allow molten sulfur to flow back into the high temperature reaction zone while the reversed gas flow reopens the flow channels.

7. The method of claim 1 for shifting the chemical reaction to the desired end products wherein the temperature and pressure of the reaction is controlled by varia-

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tions in at least one of oxidizing agent, oxygen content thereof, gas withdrawal and injection rates.

8. The method of claim 1 wherein permeability to injected gas is maintained when liquid sulfur starts to solidify in the flow channels ahead of the high temperature zone by back flowing the injection well on an intermittent basis to allow molten sulfur to flow back into the high temperature reaction zone while the reversed gas flow reopens the flow channels.

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References Cited

UNITED STATES PATENTS

531,787	1/1895	Dubbs	299—5
1,259,537	3/1918	Lucas et al.	29—5
2,688,464	9/1954	Payne	175—12
3,131,914	5/1964	Miller	299—5

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