

United States Patent

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[54] **SULFUR EXTRACTION BY SEQUENTIAL CONTACT WITH VAPOR AND WITH LIQUID PERCHLOROETHYLENE**
6 Claims, 2 Drawing Figs.

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C01d 17/08

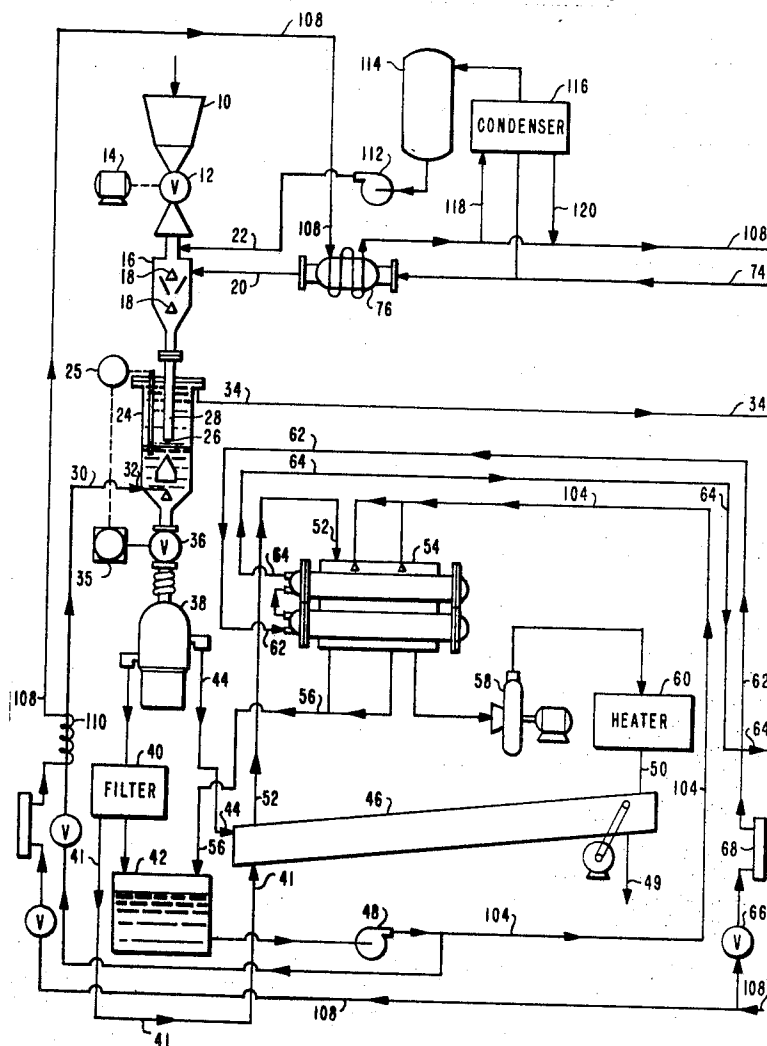
[50] Field of Search **23/312,**
309, 299, 300, 224, 225, 229, 308 S, 312 S

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ABSTRACT: This patent describes a process for the recovery and purification of sulfur which comprises contacting a sulfur-bearing ore with hot perchloroethylene vapor, permitting at least some of said vapor to condense on said ore particles, contact said ore with liquid perchloroethylene in an extraction zone whereby a substantial portion of the elemental sulfur in said ore is extracted into said perchloroethylene phase, and thereafter recovering said elemental sulfur from said perchloroethylene phase. Preferably the perchloroethylene used in the practice of the process is combined with a perchloroethylene stabilizer which retards the decomposition of the perchloroethylene.



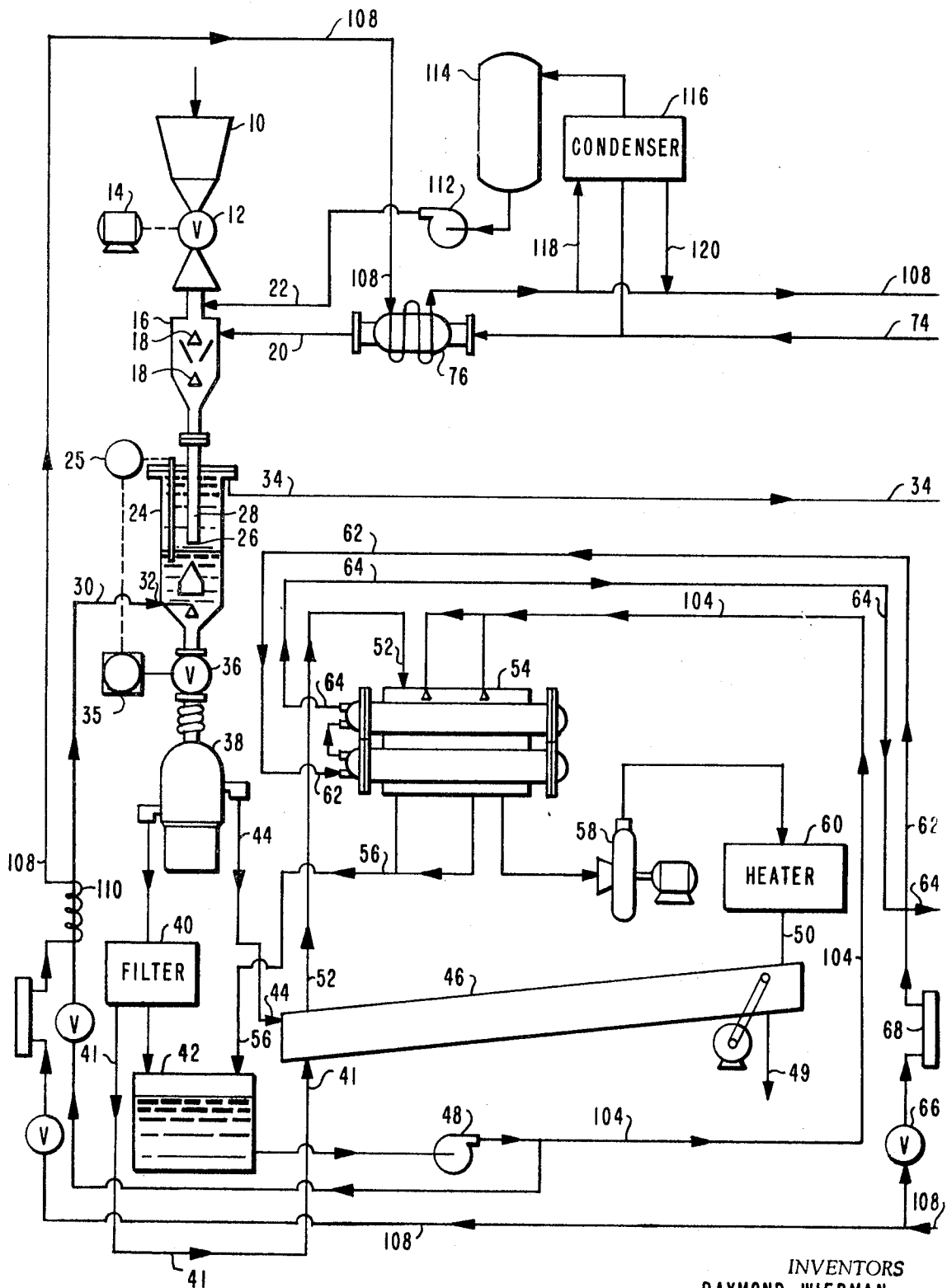


FIG. -1A

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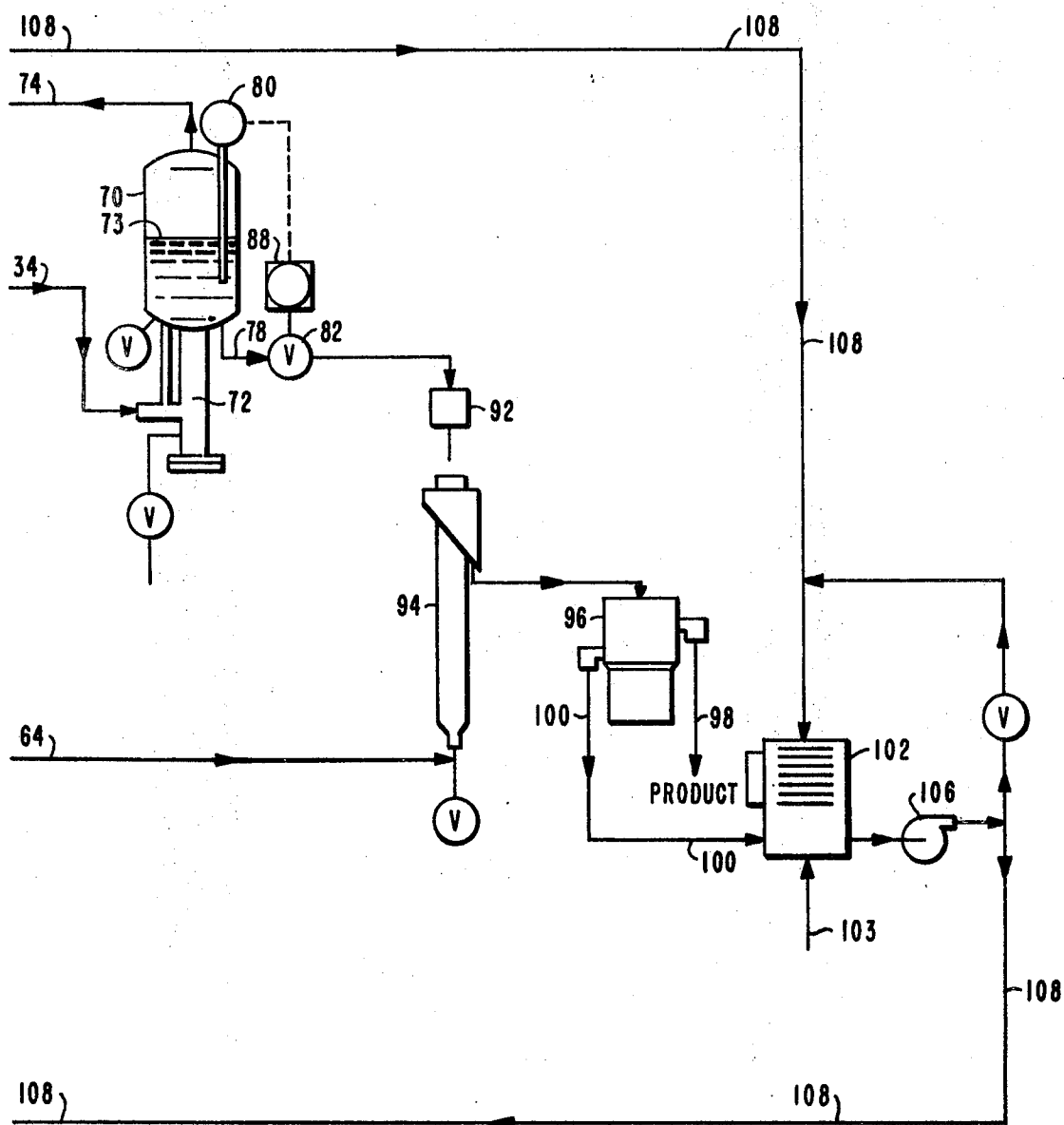
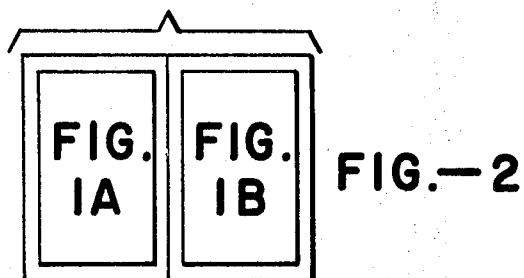


FIG.-1B

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SULFUR EXTRACTION BY SEQUENTIAL CONTACT WITH VAPOR AND WITH LIQUID PERCHLOROETHYLENE

BACKGROUND OF THE INVENTION

The field of the present invention pertains to the recovery and purification of elemental sulfur from sulfur-bearing ore.

Recently it has become increasingly apparent that the world supply of sulfur susceptible to recovery by the well-known Frasch process is rapidly diminishing and that it is unlikely that the future requirements for sulfur can be satisfied from present sources by the Frasch process. Accordingly, there has been an intense interest in the exploitation of other sulfur-bearing materials as a source of elemental sulfur. One such approach involves the use of perchloroethylene to extract sulfur from sulfur-bearing ores. However, this process has not been successful since the extraction is relatively inefficient and there is a tendency for the perchlorethylene to become tarry and a contaminant in the process after a period of time. The present invention is specifically directed toward the improvement of this process and for the first time making perchloroethylene a feasible material for use in the extraction of sulfur. In this connection various other solvents have been proposed for the extraction of sulfur including various hydrocarbons, both aliphatic and aromatic. Generally these materials are not suitable for extraction because of their inflammability and also because most of them are relatively poor extractants for sulfur because of their low dissolving power on sulfur. Therefore, it is necessary to use large volumes of these hydrocarbon solvents which increases the handling, pumping costs and equipment costs.

SUMMARY OF THE INVENTION

Briefly, the present invention comprises a process for the purification of sulfur which comprises contacting a sulfur-bearing ore with hot perchloroethylene vapor, permitting at least some of said vapor to condense on said ore particles, contacting said ore with liquid perchloroethylene in an extraction zone whereby a substantial portion of the elemental sulfur in said ore is extracted into said perchloroethylene phase, and thereafter recovering said elemental sulfur from said perchloroethylene phase. Preferably the perchloroethylene used in the practice of the process is combined with a perchloroethylene stabilizer which retards the decomposition of the perchloroethylene.

It is an object of the present invention to provide an improved process for the recovery of elemental sulfur from sulfur-bearing ore.

More particularly it is an object of the present invention to provide for a new method for the removal of sulfur from sulfur-bearing ores utilizing perchloroethylene first in a vapor form and then in a liquid form.

Still another object of the present invention is the provision of an efficient method for the recovery of sulfur from sulfur-bearing ores in which the volume of solvent is minimized and there is essentially no hazard or danger of an explosion being present.

Yet another object of the present invention is the provision for the means for the utilization of perchloroethylene in the recovery of sulfur without the development of tars and gums which have heretofore plagued the art.

These and other objects and advantages of the invention will be apparent from the more detailed description which follows.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The sulfur-bearing ores are prepared in a conventional manner such as by reducing material through several stages of crushing generally to a size of about -6 to -8 mesh. At this size it has been found that the porosity of the matrix and dissemination of the sulfur particularly facilitates the liberation and exposure of the sulfur. Reduction of ore to this size by several stages of crushing is quite common in the mining industry. Generally since this type of rock has a low-work index,

two-stage closed circuit dry crushing utilizing jaw or gyratory crushers for the primary stage and impactors or hammermills for the secondary stage are sufficient to obtain this size distribution. This type of crushing circuit is substantially the same as that employed in the potash industry to prepare process feed of the same size. Accordingly, it is not necessary to discuss the apparatus utilized in this invention for particle reduction in any greater degree since this apparatus is already familiar to those skilled in the art. However, the present invention is particularly notable in that the perchloroethylene used in the sulfur removal is available, either in liquid or vapor, to control and prevent fines resulting from dusting in the grinding operation or subsequent handling of particulate material.

It has been found that reduction to finer sizes does not accelerate dissolution and, in fact, the production of the finer materials either requires added filtering, or in the absence of such filtering, tends to retard separation of the perchloroethylene from the gangue in the subsequent separation phase of the process.

The crushed ore is withdrawn continuously from a bin through a rotary valve which acts as a controlled rate constant displacement feeder and as a gas lock to prevent the escape and loss of organic vapor through the bin. The rotary valves are capable of sustaining feed rates of several hundred tons per hour in larger sizes. As the ore discharges from the feeder and enters a hermetically sealed reactor, it is contacted by hot solvent vapors of perchloroethylene from the liquefier which, upon condensing at contact, effect partial dissolution of the sulfur and the ore. In addition, hot perchloroethylene solvent is pumped into the four quadrants of the feed and of the vertical primary reactor to slurry new feed and improve its entry rate into the reactor. Mechanical agitation is normally not required in transfer of material from stage to stage but is generally affected entirely by gravity. Dissolution of the sulfur, it has been found, is virtually complete within the primary reactor.

The reactant slurry enters the secondary reactor which functions as a separator vessel as well as completing dissolution of sulfur by standpipe, displacing the clear and pregnant supernatant perchloroethylene solvent at the top of this vessel to the liquefier.

The second slurry, now composed of barren matrix and cool pregnant perchloroethylene solvent, is withdrawn at a controlled rate from the discharge cone of the secondary reactor by gravity and continues to a screen, preferably an oscillating screen fitted with a stainless steel cloth with a fine enough weave to permit rapid pass through of perchloroethylene solvent while retaining most of the gangue. In lieu of the oscillating screen, a vacuum filter or other liquid-solids separating device can be used. At this point the perchloroethylene solvent and barren matrix are cool.

The screen oversize product or tailings, discharges to a dryer operated at temperatures sufficiently high to boil off residual solvent. Exhaust fans, located at the discharge end of the dryer, pump the vapors to a surface condenser which may utilize water or, preferably, recycled solvents as the cooling medium. In this manner, heat of evaporation is recovered and utilized to preheat recycling solvents.

The pregnant solvent displaced from the secondary reactor enters the liquefier by gravity. Since the hot vapor is continuously withdrawn from the liquefier and enters the first reactor under its own pressure, it can be seen that precipitation of the solvent occurs due to supersaturation of the solvent due to the introduction of heat and boiling of the solvent. The liquefier is normally operated at atmospheric pressure. In the event a solution of sulfur is withdrawn from the liquefier, it is treated in essentially the same manner as the tailing for solvent recovery. If molten sulfur is recovered from the liquefier, no further solvent remains to be removed. The small amount of sulfur recirculating with the solvent from the product screen is of little consequence.

Turning to the drawings:

FIG. 1A is a flow sheet of the initial phases of the process of this invention; and

FIG. 1B is a flow sheet of the final phases of the process of the invention.

FIG. 2 is the composite of FIGS. 1A and 1B.

The crushed ore is loaded into hopper 10. The effluent from hopper 10 is controlled by rotary valve 12 operated by motor 14. The ore passes through valve 12 into contactor 16 which is provided with static contactor members 18. Hot perchloroethylene vapor is introduced via line 20. Optionally, the ore surface may be prewetted with liquid perchloroethylene from line 22. In any event, some of the vapor condenses on the ore which then passes to the extraction zone, in this case, leach tank 24. The ore discharges at the end 26 of pipe 28. Hot liquid perchloroethylene is continuously introduced via line 30 at point 32 so that the ore and solvent pass in a countercurrent relationship to each other. The liquid perchloroethylene bearing the extracted sulfur is removed through line 34 for recovery. The gangue or tailings are removed at the bottom of tank 24, passed through valve 36 into screen 38 where the gangue is screened to remove the bulk of the entrained and surface perchloroethylene solvent. The flow rate through valve 36 is controlled by interface controller 25 and actuator 35. The perchloroethylene solvent recovered in screen 38 is filtered in filter 40, and collected in surge tank 42. The filter cake from filter 40 is passed via conduit 41 to dryer 46 for solvent recovery. The gangue is passed via conduit 44 to dryer 46. A portion of the perchloroethylene collected in tank 42 is recycled by pump 48 via line 30 to leach tank 24. The gangue in dryer 46 is dried with the dried gangue being removed as waste via line 49. The perchloroethylene is evaporated in the dryer 46 by a hot airstream introduced via line 50 and removed via line 52. The perchloroethylene in the airstream is removed in heat exchanger 54. The perchloroethylene recovered in heat exchanger is returned to surge tank 42 via line 56. The hot air for the dryer is continuously circulated by blower 58, with heat being supplied by heater 60. The cooling in heat exchanger 54 is supplied by water from inlet 62. The water is removed from the heat exchanger via line 64. The flow of water to the heat exchanger 54 is regulated by valve 66 and the rate determined by rotometer 68.

The sulfur-bearing liquid perchloroethylene solvent removed via line 34 to liquefier 70 which is provided with heating elements in zone 72 to evaporate the perchloroethylene. The particular sulfur recovery procedure used and the form of the recovered sulfur can be widely varied within the scope of our invention. For example, a concentrated solution of sulfur could be withdrawn at the surface 73, and cooled to yield fluffy sulfur particularly useful for agricultural uses. If such a product is desired, the liquefier 70 could also be replaced by a vacuum liquefier having a construction familiar to those skilled in the art.

In the embodiment shown in the drawings, the perchloroethylene solvent is continuously evaporated from surface 73 and returned via line 74 to reactor 76 where it may be purified before entering line 20. The elemental sulfur is recovered in molten form via line 78. The liquid level in liquefier 70 is maintained by liquid level detector 80, valve 82 and actuator 88.

The molten sulfur from line 78 passes via prill head 92 to prill tank 94 where the sulfur is prilled in a countercurrent flow of water introduced via line 64. The wet prills from tank 94 are screened in screen 96 for recovery as prilled product at discharge 98. The separated water is removed via line 100 to cooling tower 102. The cooling tower air cools the water used throughout the process shown in the drawings, although many other cooling arrangements will be obvious to those skilled in the art.

Water from water tower 102 is pumped by pump 106 to the water system. This system includes line 108 which feeds line 62 with condenser cooling water, and optionally, feeds cooling coil 110. The water system is a closed loop so that the same water is used on unit 76 and then returned to tower 102. The makeup water required to replace that loss to evaporation in tower 102 may be added through line 103.

As is indicated above, for certain ores, it is sometimes desirable to wet the ore with perchloroethylene prior to contact with the vapor. This can be accomplished by pumping liquid perchloroethylene via pump 112 from tank 114. The liquid perchloroethylene is obtained by condensing vapor in condenser 116. The cooling water for the condenser 116 is withdrawn from line 108 through line 118 and returned via line 120.

Many variations are possible in the process described above. For example, in lieu of contactor 16, a screw conveyor or other contacting device may be used.

The extraction temperature in leach tank 24 is preferably between about 220° F. and 251° F., the boiling point of perchloroethylene. By injecting cool perchloroethylene via line 28 at the lower end of tank 24, a thermal gradient is maintained across the ore bed in the tank. Thus, the ore at the bottom of the tank is the coolest portion of the ore within the tank. By the time the ore reaches screen 38, it has normally cooled to about 100° F., which minimizes the amount of sulfur dissolved in the perchloroethylene leaving the screen, hence diminishing the possibility of crystallization and clogging of pipes.

In general, the hot air introduced via line 50 to dryer 46 is at a temperature of about 350° F., and leaves the dryer through line 52 at about 160° F. This temperature condition adequately evaporates the perchloroethylene from the gangue.

Various means may be used to clean the tubes in heat exchanger 54. For example, as shown in the drawing, perchloroethylene solvent may be passed through line 104 and sprayed onto the tubes.

The present invention provides for unusual thermodynamic and mechanical efficiency. Not only is a closed water system possible for providing the necessary cooling throughout the system, but other savings are possible. For example, the gangue from line 49 may, if desired, be used to preheat the ore before it is introduced into hopper 10. In this way, the surface and entrapped moisture present in the ore is substantially removed, which reduces undersired frothing and foaming in leach tank 24.

In the preferred embodiment of our invention, the perchloroethylene contains an effective stabilizing amount of a stabilizer such as a nonionic surfactant, an alkyl arylsulfonate, or a lower alkanol such as methanol and ethanol. The stabilizer permits recycle of the same perchloroethylene for prolonged periods of up to 2 or 3 months, or more, and provides an important saving of solvent. In general, the stabilizer is used in an amount up to about 5 percent by weight of the perchloroethylene.

The liquefier 70 contains molten sulfur. The heating elements in zone 72 normally have a surface temperature of 316° F. or less. Higher temperatures are to be avoided since at said temperature, sulfur converts to the mu form which is black and discolors the product.

The prills formed in tank 94 preferably are about 1/8 inch in diameter or less to provide for a bright yellow color, called for by many sulfur specifications. It is to be understood, however, that the final form of the sulfur liberated from the ore according to this invention may take numerous different forms, depending on the end use intended for the product.

The reactor 76 basically provides a zone of purification for the perchloroethylene vapor. To aid in this purification, reactor 76 may contain absorbents, adsorbents, and other materials commonly used to remove small amounts of contaminants from vapors.

Those skilled in the art will immediately recognize the many advantages of the described process. The process is safe, and utilizes closed systems for recycling perchloroethylene, water and air. The system is capable of continuous operation for long periods without changing these materials. Further, the process is adapted to produce sulfur in any commercial form. The invention is applicable to any form of ore containing elemental sulfur. It will also be recognized by those skilled in the art that this invention has no application to the recovery of any chemically combined sulfur such as is present in pyrites.

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Having fully defined the invention it is intended that it be limited only by the lawful scope of the appended claims.

1. A process for the extraction of sulfur from particulate sulfur bearing ore which comprises sequentially (1) contacting said ore with hot perchloroethylene vapor, permitting at least a portion of said vapor to condense on the particles of said ore; (2) in an extraction zone, contacting said ore with liquid perchloroethylene in addition to that formed by condensation, whereby a substantial portion of the sulfur in is extracted into said perchloroethylene, said vapor and liquid perchloroethylene being separately introduced into said ore; (3) removing from said zone perchlorethylene containing extracted sulfur; and (4) recovering molten elemental sulfur by heating the sulfur-containing perchloroethylene removed from said zone to evaporate perchloroethylene therefrom, the vapor introduced into said ore being comprised of vapor formed in said evaporating step.

2. The process of claim 1 wherein molten sulfur formed in

the course of said evaporation is prilled.

3. The process of claim 1 wherein said liquid and vapor perchloroethylene contains an effective stabilizing amount of a stabilizer selected from the group consisting of alkyl aryl sulfonates and nonionic surfactants.

4. The process of claim 3 wherein said stabilizer is a nonionic surfactant.

5. The process of claim 1 wherein said ore is passed through said extraction zone countercurrent to and in contact with said liquid perchloroethylene.

6. A process according to claim 1 wherein gangue is removed from said extraction zone and liquid perchloroethylene is separated therefrom the recycle to said zone, and wherein the residual perchloroethylene in said gangue is evaporated therefrom and recycled for condensation on said ore.

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