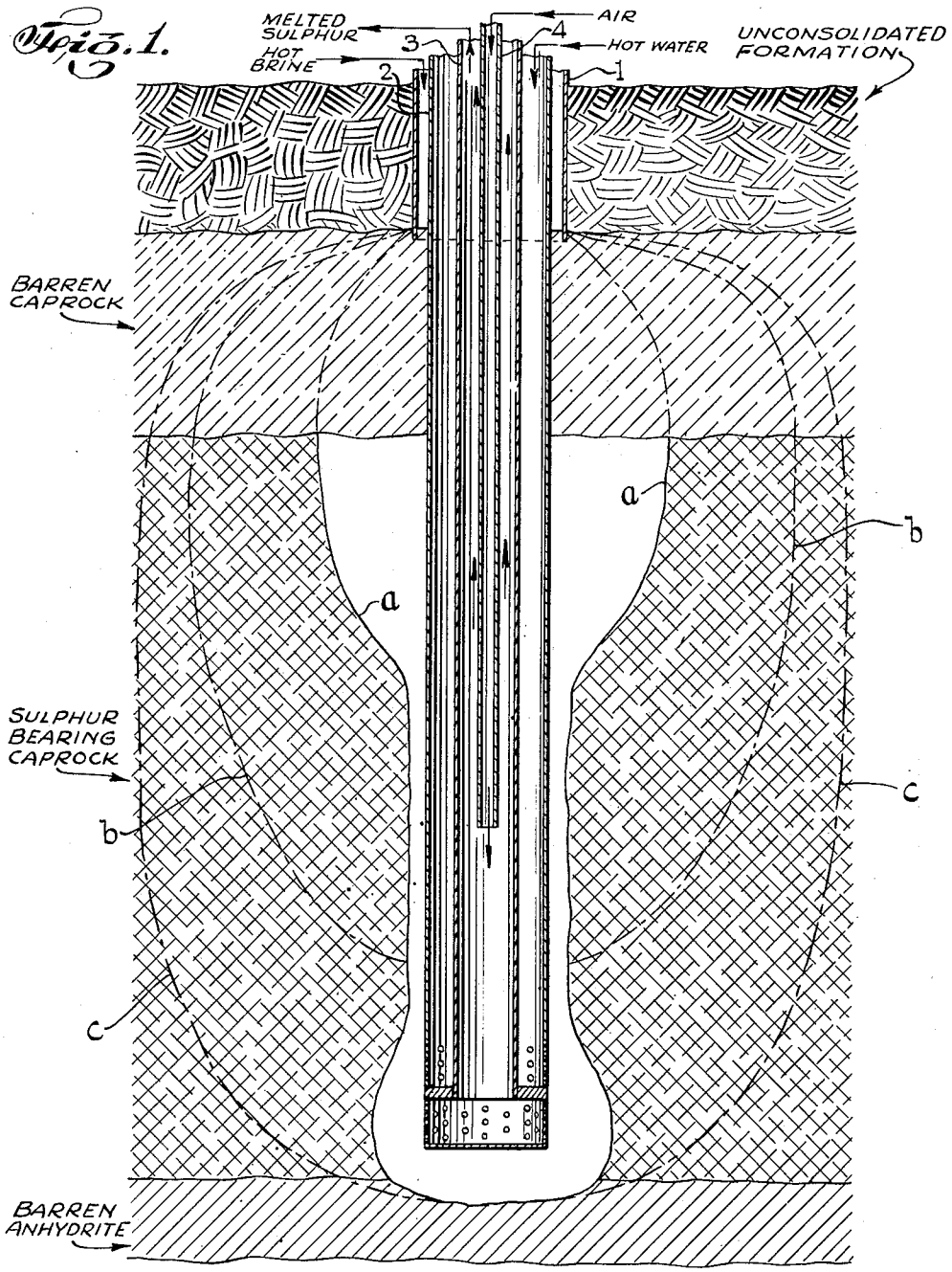
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MINING OF SULFUR

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Fig. 1.



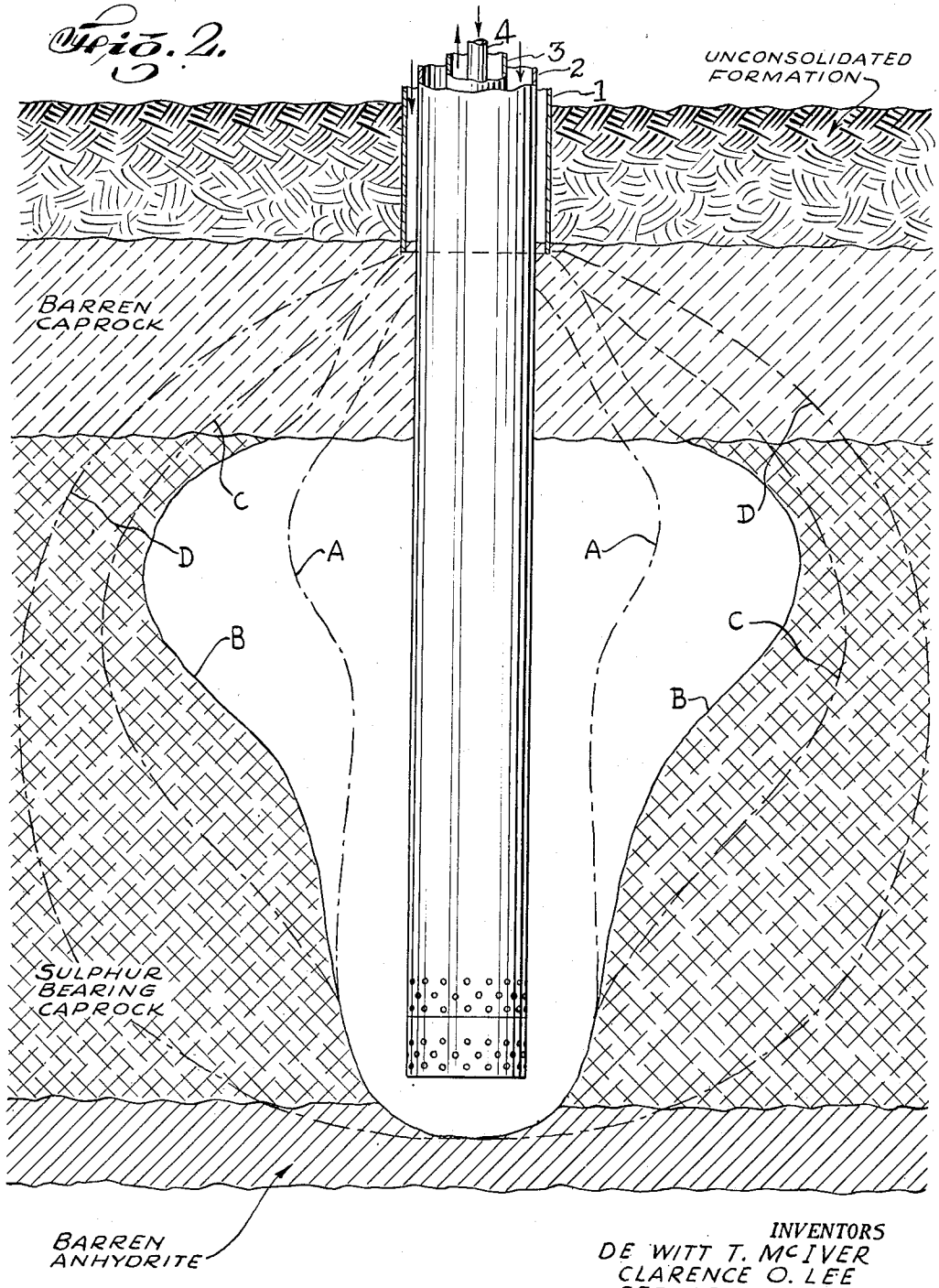
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Fig. 2.



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MINING OF SULFUR

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This invention relates to methods of mining sulfur, the same constituting improvements upon the well-known hot water mining or Frasch process, and has for an object the recovery of larger amounts of sulfur from sulfur deposits than can be recovered by the ordinary and special practices of the Frasch process, and as another object, the recovery of sulfur from deposits which respond inadequately or not at all to such known practices.

In the mining of sulfur by the conventional Frasch process, hot fresh water is introduced at or near the bottom of the sulfur formation or just above the level at which the melted sulfur is expected to collect in a pool. The water introduced maintains the sulfur pool in a molten condition and due to its lower specific gravity than the water in the surrounding formation, flows upwardly and to a smaller extent, outwardly, thus heating the formation in a funnel shaped area at a progressively higher and higher level, and when the temperature in the path of the water is sufficiently raised, the sulfur present in the hot area is melted to a liquid flowable state, and due to the action of gravity, it flows downwaardly in the heated region in the direction of, and to, the pool at the bottom of the well. From this pool, the sulfur is withdrawn or forced to the surface of the mine by the action of warm compressed air.

Whereas this process leads to good recovery of sulfur from many formations, it does not work satisfactorily in many instances. In some formations, the introduction of the usual amount of water at the usual temperature results in little or no accumulation of sulfur in a pool from which it can be withdrawn. From such formations, fair amounts of sulfur can, and have heretofore been, recovered by a modified operation involving introducing very substantial amounts of hot water for a period of days during which time no sulfur accumulates in the pool for withdrawal, and then reducing the amount of water introduced to the usual volume whereupon sulfur accumulates in the pool and can be withdrawn over a period of several days. During this period of days, the amount of sulfur in the pool gradually decreases until no more can be withdrawn and productivity can be obtained again only by repeating the introduction of the very large quantities of water for an additional several-day period.

This type of well is expensive to operate, for it employs a larger amount of heat and water and recovers from the well a smaller quantity of sulfur than from normal mines. The processes of

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the present invention may be applied with particularly beneficial results to this type of formation but are equally applicable for obtaining increased yields from the usual type formation wherein the ordinary hot water mining process can be successfully employed.

Two variations in operation of the invention are hereindescribed. The first embodiment of the process is of particular value in formations which do not respond adequately to known Frasch operations and where increased rates of flow of hot water prevent sealing of the molten sulfur. The second embodiment is of value in the recovery of sulfur from all of the usual types of formations encountered and leads to increased yields by melting and collecting the sulfur from a larger area than is possible by present known processes.

According to the first embodiment of the invention, hot brine or other heavy aqueous solution is introduced into the sulfur formation at a high level in the sulfur stratum with the result that the sulfur is melted in a progressively downward direction, the melted sulfur and hot solution flowing in a concurrent direction, the sulfur collecting in a pool at a lower lepel in or below the sulfur formation from which it is removed by the conventional air lift. This concurrent flow of hot solution and molten sulfur is obtained by the introduction under pressure at a relatively high point in the sulfur stratum, preferably near its top, above, at, or slightly below its upper limit, of a heavy brine or other aqueous solution having a higher specific gravity than the mine water at any temperature above about 230° F., as at the temperature the brine is introduced or at a somewhat lesser temperature.

In this first embodiment, the sulfur melted by the hot solution may be collected at and withdrawn from the bottom of the melting zone which is continuously moving downwardly, but it is preferably collected and withdrawn from near the bottom of the sulfur formation. The flow of melted sulfur (and hence also the hot solution from the melting zone initially near the top of the formation) to the collecting pool at some lower position in or at the bottom of the formation is effected or facilitated by creating a hot channel preferably around an uninsulated heated pipe extending through the melting zone to the bottom of the mine. This pipe may be heated by any suitable fluid introduced inside it, and the heat conducted therefrom into the surrounding sulfur formation will melt the sulfur imbedded there and permit the same as well as the sulfur melted

by the hot solution to flow to the bottom end of the pipe where the sulfur will collect in a pool. The pipe and zone surrounding the same may be effectively heated by a relatively small amount of fresh hot water or light aqueous solution preferably discharged from the heating pipe substantially at its bottom end in the sulfur collecting zone just above or in the sulfur pool. The water or other solution discharged from the pipe also maintains the sulfur in the pool in the melted state. This pipe may also contain inner concentric pipes for compressed air and for the withdrawal of the melted sulfur.

The hot water introduced at the bottom of the mine is preferably fresh water or water to which no salt has been added. Through the use of fresh water in concentric pipes several outstanding advantages are obtained. The fresh hot water possesses a lower specific gravity than the mine water and hence upon flowing from the end of the pipe at the sulfur pool it rises upwardly around and in contact with the outside of the pipe and protects it from the corrosive action of the sulfur in the pool and of the hot brine descending with the molten sulfur to the pool at the bottom of the mine.

Tests have proven that the use of fresh water in this pipe has the additional outstanding advantage of partially purifying the sulfur by its dissolving action on the impurities in the countercurrent flow of sulfur, the said impurities remaining with the water instead of being carried out in the sulfur. Finally, by using fresh water instead of brine in this pipe, any leakage through holes or around the threads of the couplings into the pipe will not cause contamination of the sulfur flowing from the mine inside the pipe.

Where the formation is such that an excessive amount of fresh water introduced at the bottom interferes with the ready flow of the molten sulfur in its downward passage to the pool at the bottom of the mine, the amount of fresh water or other light liquid introduced at the lower level should be relatively small as compared with the amount of brine or heavy liquid introduced near the top of the sulfur formation.

This first embodiment is illustrated in Figure 1 of the accompanying drawing wherein there is diagrammatically shown a sulfur well including a casing 1, suitably of ten-inch diameter, extending through an unconsolidated formation and terminating within but near the top of barren caprock, in which casing the heavy aqueous solution or salt brine is conducted and from which it is discharged to flow outwardly and downwardly into the sulfur formation. In some instances, termination of the casing 1 just above the sulfur bearing caprock has given better results. Within this casing 1, there is a pipe 2, suitably of eight-inch diameter, for the introduction of hot water or other light solution extending through the barren caprock and having a number of holes at its lower end, in about the last three to twenty feet thereof. A pipe 3, suitably of four-inch diameter for the removal of sulfur is concentrically situated within the pipe 2 and terminates one to several feet above the bottom of pipe 2. Concentrically within the pipe 3 there is a pipe or air line 4, suitably of one and a quarter inch diameter, for the introduction of air for lifting the sulfur within the pipe 3 in the conventional manner.

In operating the described mine, substantial amounts of a hot sodium chloride brine of 10–20 per cent concentration (e. g., a 16 per cent solution) at a sulfur melting temperature is introduced through the ten-inch casing 1 and discharged into the barren caprock. From the point of introduction, the brine spreads outwardly and downwardly and early in the well life appears to melt the sulfur in the upper part of the area indicated generally by the line *a*. During the introduction of the hot brine, a substantially lesser amount of an aqueous solution, preferably hot fresh water, also at a sulfur melting temperature is introduced through the pipe 2 and out through the perforations into the lower part of the sulfur bearing caprock. The heat of the hot water conducted through the walls of pipe 2 together with that of the discharged hot water appears to cause the sulfur in the lower part of the zone bounded by the line *a* surrounding the pipe 2 to melt and flow downwardly into a pool near the end of said pipe, this pool preferably being formed at the bottom of the sulfur bearing caprock or alternatively, either wholly or partially within the barren anhydrite strata below the sulfur bearing caprock.

During continued operation of the mine, the hot brine solution progressively melts the sulfur outwardly and downwardly in the area bounded by the line *b* and ultimately in the area bounded by the line *c*. From the pool at the bottom of pipes 2 and 3, the sulfur is continuously withdrawn in conventional manner with the aid of the air lift up the pipe 3 and out of the mine.

In this embodiment, the ratio of the hot brine introduced in the casing 1 to the hot fresh water introduced through the pipe 2 at the lower level in the mine may be varied to suit particular formation conditions, but ordinarily, a substantially major proportion of the liquid is introduced through the casing 1. Good recoveries of sulfur were maintained when the amount of hot brine introduced at the high level was several hundred gallons per minute and the amount of hot fresh water introduced through the pipe 2 at the bottom of the mine was maintained at as little as fifty gallons per minute. The well operated in this manner quickly became a prolific and economical producer of sulfur.

The effectiveness of the above process was readily proven by comparing the results obtained with those results following a discontinuance of the flow of brine through the casing 1. When the introduction of hot brine in the pipe 1 was stopped, the introduction of hot water in the pipe 2 even in large amounts would not cause the sulfur to seal in the pool such that it could be withdrawn through pipe 3.

In accordance with the second embodiment of the invention, of even more importance in sulfur formations of the type ordinarily encountered than the first embodiment, the amount of hot fresh water or light solution introduced at the lower level in the mine is greater than in the first embodiment and may be much greater in proportion to the amount of hot brine or other heavy liquid introduced at the higher level in the mine. Excellent results are ordinarily obtainable by proportioning the total water supplied equally between the heavy liquid at the higher level and the light liquid at the lower level. The opposing action of the descending heavy liquid and ascending light liquid apparently causes a greater horizontal flow of either or both liquids and effects melting of the sulfur in the formation throughout a much greater area than when all the water introduced is of the same gravity or when all is introduced at one level in the formation.

Increased yields of sulfur are obtainable by apportioning the water in other than equal amounts as 60 to 40 or 40 to 60 and even 80 to 20 or 20 to 80. When the amount of either the heavy liquid or the light liquid is made too small, the practical improvement in yields becomes negligible. The amount and proportion of each liquid apparently must be sufficient to cause some extra outward flow of both or either of the hot liquids.

This second embodiment is diagrammatically illustrated in Figure 2 of the drawing. The pipes are arranged the same as or similar to those of Figure 1. The simultaneous introduction of the heavy brine or liquid at the top and the hot water or other light solution at the bottom both in substantial amounts causes flow and melting of sulfur, during the early life of the well, in the area bounded by the line A. As the operation of the mine continues, the field of sulfur removal apparently spreads progressively outwardly within the area bounded by the line B, then to the area bounded by the line C, and finally to that bounded by the line D. Since the area bounded by the line D is substantially greater than the area that can be heated by the introduction of water or brine alone, the yield of sulfur is greater through the practice of the present invention. Best results are frequently obtained when the substantial amounts of the hot brine and hot water meeting in the formation are such as to provide a mixture having a specific gravity approximately equal to that of the formation water, for in that case, the flow tendency appears to be one which spreads in the melting zone in all outward directions.

In some mines, a combination of the processes of the two embodiments gives best results, the combination involving first introducing substantial amounts of brine at the top and small amounts of water at the bottom of the mine, and then after a period either gradually or suddenly adjusting the flow of the two heating liquids to equal volumes.

Laboratory experiments on glass enclosed models of sulfur wells and actual operation of sulfur mines both fairly conclusively indicate that the flow of brine and hot water and the melting of sulfur progress in the manner hereinbefore described. The invention as claimed herein, however, is not limited by any theory of operation.

The density of the hot "heavy" liquid introduced in the top of the sulfur formation may be varied within wide limits, it being necessary only that it be greater than that of the formation water at all brine temperatures employed in the operation. If light brine or other aqueous solution other than fresh hot water is introduced at the lower or bottom level of the sulfur formation, its density also may be varied within wide limits, for any liquid that is hot enough will heat the formation around the pipe 2 and also maintain the sulfur in the pool in a molten condition. The density of both these solutions, naturally should be adjusted to provide the most desirable operating conditions for the particular formation being mined.

No novelty is herein claimed in the use of brines broadly in sulfur mining for both hot and cold brine respectively have been suggested for introduction into the bottom of sulfur mines to effect or facilitate sulfur recovery. As far as we are aware, no one heretofore has proposed either the introduction at a high level of a hot brine or other aqueous liquid heavier than the mine water such that the hot brine flows downwardly with the sulfur melted by it which is collected at a lower level, or the simultaneous introduction of such hot brine at a high level and of hot water or other light solution at a lower level at which the sulfur is collected in a pool for withdrawal from the mine.

The hereindescribed mining equipment may be varied considerably without departing from the principles of the present invention. The pipe sizes may be varied as well as the distance between the ends of the several pipes. Furthermore, an additional pipe slightly smaller in diameter than the casing 1 may be employed between the casing 1 and the pipe 2 to introduce the brine and prevent its contact with and corrosion of the permanently installed casing 1.

Whereas the process of the present invention has been described somewhat in detail, it should be understood that the invention contemplates all methods by which its principles may be put into operation, as defined by or within the scope of the accompanying claims. In these claims, the terms "heavy" and "light" referring to the respective hot liquids or aqueous solutions define their specific gravities as related to the mine water in the mine being operated.

We claim:

1. In the mining of sulfur involving the use of hot water under pressure in a sulfur well, the improvement which comprises, introducing a hot aqueous solution having a specific gravity greater than that of the mine water at a superior level in the well, introducing hot water at an inferior level in the well below the midpoint of the distance between the level at which the solution is introduced and the level of the melted sulfur in a pool in the well and collecting the sulfur melted by said solution and by said hot water in said pool at the bottom of the well from which the sulfur is withdrawn to the surface.

2. In the recovery of sulfur by the hot water mining process, the improvement which comprises, introducing hot heavy brine at a high level in the mine to melt sulfur at that level and progressively in an outward and downward direction, simultaneously introducing hot water at a lower level to melt sulfur at that level and adjacent to the pool of sulfur which collects in the well and progressively in an outward and upward direction, collecting the resulting melted sulfur at a low level and withdrawing the same to the surface.

3. In the recovery of sulfur by the hot water mining process, the improvement which comprises, introducing a hot aqueous solution having a specific gravity greater than that of the mine water substantially at the top of the sulfur formation, simultaneously introducing hot water substantially at the bottom of the sulfur formation in such manner as to heat the sulfur in the formation in the vicinity of the sulfur pool formed in the well thereby maintaining the pool in molten condition, creating a passage for the flow of melted sulfur from said high level to said low level by heating the formation therebetween to a sulfur melting temperature and collecting the sulfur melted by the hot solution and the hot water substantially at the bottom of the well from which the same may be removed in conventional manner.

4. In the mining of sulfur involving the use of hot water under pressure in a sulfur well, the improvement which comprises, introducing a major portion of the hot water in the form of an aqueous brine solution having a specific gravity greater than that of the mine water at a superior

level in the well, introducing a minor portion of the hot water at an inferior level in the well below the mid-point of the distance between the level at which the brine is introduced and the level of the melted sulfur in a pool in the well where the sulfur melted by said solution collects in a pool before being withdrawn from the well.

5. In the removal of sulfur from sulfur formations by the hot water mining process in pipes within a pipe, the improvement comprising, introducing hot heavy brine into a pipe terminating near the top of the sulfur formation, introducing lighter hot water into another pipe terminating below the end of said first-mentioned pipe and below the mid-point of the distance between the terminus of the first mentioned pipe and the level in the pool in which the sulfur collects, and removing the sulfur melted by said brine and water which collects in said pool at the bottom of the well, by means of a pipe terminating near said bottom.

6. In the mining of sulfur by the hot water process in concentric pipes, the improvement which comprises, introducing hot heavy brine into the sulfur formation by means of an outer pipe terminating near the top of the sulfur layer to be mined, introducing light hot water into the sulfur formation by means of a second concentric inner pipe terminating at a lower

point in the sulfur layer below the mid-point of the distance between the terminus of the outer pipe and the level of the sulfur which collects in a pool, withdrawing sulfur melted by said brine and water by means of a third concentric inner pipe terminating in the pool of melted sulfur, assisting the sulfur elevation in said third pipe by means of air introduced into said third pipe by a fourth pipe terminating near the bottom end of said third pipe.

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