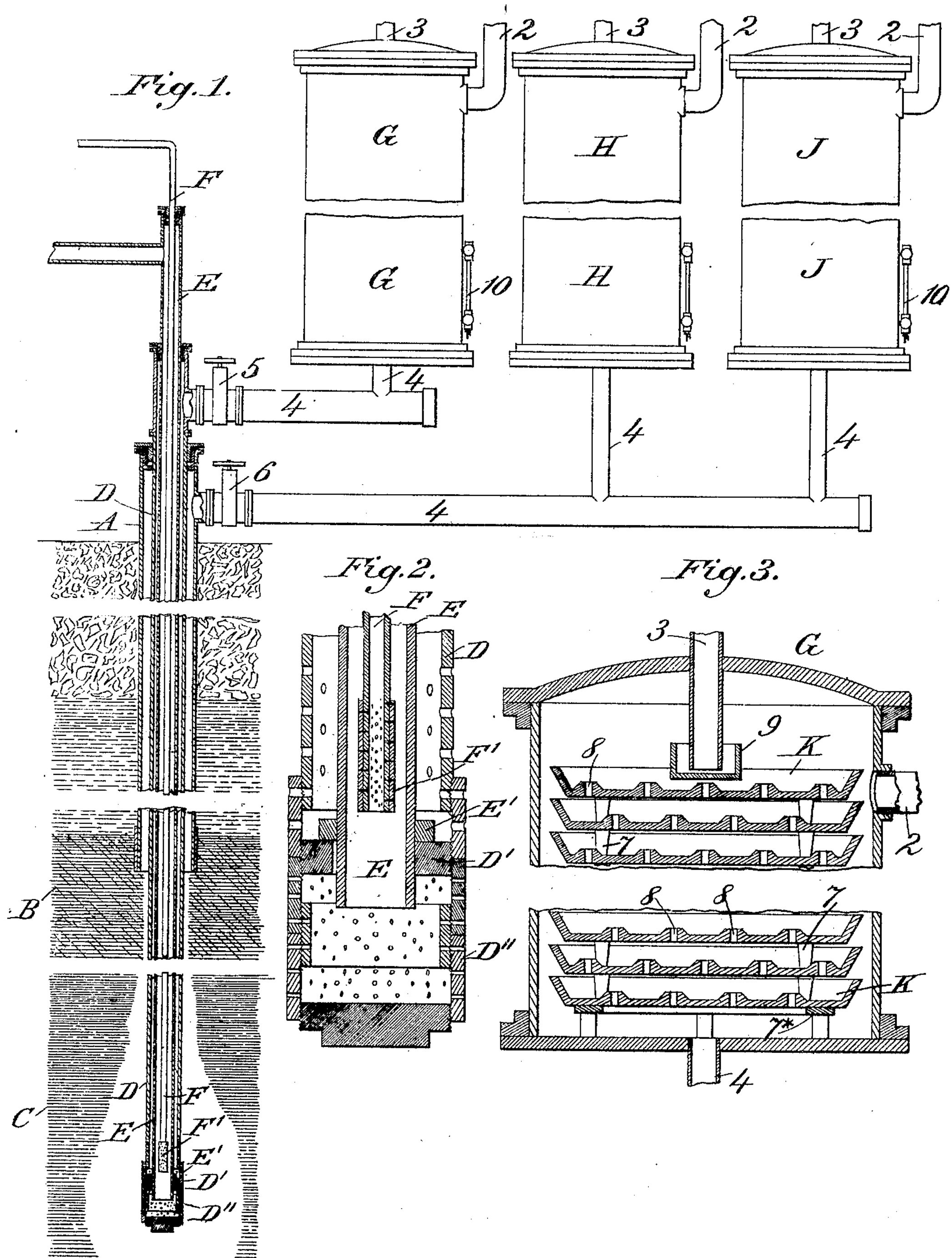
No. 799,642. PATENTED SEPT. 19, 1905.

H. FRASCH.

PROCESS OF MINING SULFUR.

APPLICATION FILED MAY 27, 1897.



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UNITED STATES PATENT OFFICE.

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PROCESS OF MINING SULFUR.

No. 799,642. Specification of Letters Patent. Patented Sept. 19, 1905.

Application filed May 27, 1897. Serial No. 638,357.

To all whom it may concern:

Be it known that I, HERMAN FRASCH, a citizen of the United States, residing at Cleveland, in the county of Cuyahoga and State of Ohio, have invented certain new and useful Improvements in Processes of Mining Sulfur; and I do hereby declare the following to be a full, clear, and exact description of the invention.

This invention relates more particularly to the removal of sulfur from deposits in the earth which consist of or contain free sulfur by fusing the sulfur in the underground deposit and raising it in a melted condition; but some of the improvements admit of a wider application, and each of them is intended to be secured for all the uses to which it may be adapted.

Heretofore I have secured Letters Patent of the United States No. 461,429, dated October 20, 1891, for the recovery of sulfur by the process above indicated, the fusing being effected (as more particularly described in said patent) by the circulation through the deposit of water heated under pressure to above the melting-point of sulfur, the water being returned to the surface of the ground while still above said melting-point. At the time of said patent it was considered best for the entering water to have a temperature approximating the melting-point, since melted sulfur darkens and thickens with increase of temperature. The patent names 280° Fahrenheit, which is about the temperature of steam at a pressure of thirty-five pounds, more or less, to the square inch above atmospheric pressure. The temperature of 235° Fahrenheit is named as proper for the returning water. To raise the melted sulfur, the patent describes the development of sufficient pressure in the deposit to overbalance the sulfur column by the force of the pumps sending down the hot water, the returning water being held under pressure above ground or else the use of a pump placed in the deposit to lift the melted sulfur directly. In practically applying this process a deposit of sulfur was struck from which it was found impossible to raise the melted sulfur by pressure developed in the deposit by the hot-water pumps, for the reason, as I discovered, that the porosity of the rock would allow the hot water to escape before the attainment in the deposit of sufficient pressure to overbalance the column of liquid in the sulfur-pipe. Resort was therefore had to the use of a lifting-pump in the deposit; but while possible it was found undesirable to use this mode of raising the melted sulfur, for one reason on account of difficulty with the valves. Moreover, apart from the difficulty with the pumps, the yield of sulfur was not such as had been anticipated. The smallness of the yield, I discovered, was due to water naturally present in the deposit, which limited the melting operation by its coldness and its tendency to mix with the hot water for effecting fusion. While, therefore, sulfur can be and was, in fact, obtained from a water-flooded porous deposit not only by the general process, but by one of the particular modes set forth in said patent, the difficulties in the way interfered very much with its obtainment, enhancing the cost of working and limiting the yield. The present invention while using the general process of my said patent—to wit, of fusing sulfur in an underground deposit and removing the same in the melted state—enables the operator to obtain sulfur with much less expense for a given weight and to extract larger amounts thereof from a given well than is believed to be possible with any mode described in my said patent or in my Patent No. 461,430, of even date therewith.

In accordance with the present invention instead of returning the hot water to the surface of the ground it is forced out through the porous rock, and thus even when its temperature has fallen below the melting-point of sulfur it heats the outlying rock, and so aids in maintaining a melting temperature in the cavity of the mine. Moreover, in accordance with the present invention instead of employing for fusion water of the temperature named in the patent—to wit, about 280° Fahrenheit, or, in other words, of the temperature of steam of a pressure of about thirty-five pounds to the square inch above atmospheric pressure, which temperature is below that at which melted sulfur begins to darken—water of a higher temperature is employed, its temperature being advantageously raised above that at which melted sulfur begins to darken—to wit, above 300° Fahrenheit—without being sufficient to destroy its fluidity. (See Morley and Muir's revision of *Watt's Dictionary of Chemistry*, 1894, Vol. 3, page 608.) The temperature of steam at a pressure of ninety pounds to the square inch above atmospheric pressure (which would be about 335° Fahrenheit) is suitable. By this increment in the temperature of the artificiallyintroduced water the effect of the cold water naturally present in the deposit is to that extent counteracted, so that a larger volume of the deposit (or, in other words, a larger portion of the mine) can be raised to the melting temperature of sulfur, while at the same time the fluidity of the melted sulfur is not sufficiently affected to interfere with its removal as a liquid. Also in accordance with the present invention the difficulty of raising the melted sulfur from the porous deposit is overcome by the aid of air or other aeriform fluid, (air most advantageously,) which is forced into the column of melted sulfur as near its base as may be desired and which by its presence renders the said column of air and melted sulfur of a less average density, so that the same may be raised to the top of the ground by the available pressure in the sulfur deposit. Melted sulfur is about twice the density of water, and consequently a water-pressure which may be sufficient to elevate water from the bottom of the sulfur-raising pipe to the top of the ground would lift a sulfur column only about half of that height; but notwithstanding this great disparity in density it is found that air can be introduced into the melted sulfur in such volume as to be practically useful. It may, in fact, be introduced in such volume that the average density of the air and sulfur column approximates or even falls below the density of water. In conjunction with the introduction of the compressed air or other aeriform fluid into the melted sulfur hot water is forced into the cavity of the mine in order to melt the sulfur therein and to subject the so-melted sulfur to pressure in the pool which it forms at the bottom of the sulfur-raising pipe. Further, in accordance with the present invention the hot water for fusing the sulfur is obtained by pumping or otherwise forcing water through a heater, in which it is brought into contact with high-pressure steam from a suitable generator, so that the pumped-in water is raised by the steam to an appropriate temperature for fusing the sulfur, and the water from condensation of the steam goes to increase the volume of the water for fusion. In this way the heating operation is indirect in requiring steam to be generated in one vessel and condensed in another; but it has been discovered to possess practical advantages. The generation of steam seems more efficiently to take up heat from the fire than the mere elevation of the sensible temperature of water, and besides this the heating of the water by steam condensation therein regulates itself to a certain extent automatically, since any change of temperature in the water-heater changes also the pressure therein in the same sense, so that the volume of entering steam changes automatically in the contrary sense a fall of temperature—for example, automatically resulting in a lower pressure and a larger inflow of steam, which arrests the fall of temperature. Any fall of temperature is also shown instantly by the steam-gage on the generator, so that the fire can be increased at once. The supply of hot water is obtained under the pressure of the steam, and this pressure is utilized as part of that required to force the hot water into the deposit. The hot water in the sulfur deposit is subjected constantly to the steam-pressure conveyed through the water which stands in the pipe or pipes for conveying the same down into the sulfur deposit. By this steam-pressure the column of water in the hot-water pipe or pipes may have its upper surface a considerable distance below ground, and this distance in the case of porous rock, where there is a certain natural pressure which cannot be exceeded, will depend upon the amount of steam-pressure. The pressure of steam may therefore (in such case) be increased without increasing the pressure in the mine, but simply diminishing the height of the water column in the hot-water pipe. When the maximum pressure in the rock is not thus restricted, the said pressure can be controlled by varying the steam-pressure and the hot-water column, either or both. Thus the steam may in many cases be allowed directly to heat the well for a considerable distance below ground, and in any case a supply of water of appropriate temperature and pressure can be obtained.

In order to obtain most advantageously large volumes of water heated to a high degree under superatmospheric pressure, (as required for sulfur-mining by hot-water fusion,) water-heating means have been devised which are believed to be new generally as well as in their application to sulfur-mining. In consequence, however, of official requirement of division distinguishing between water-heating, on the one hand, and mining wherein water-heating should be an element, on the other, I am not permitted to include claims herein on said water-heating means, such omission being without prejudice to my right otherwise to protect the same. In a divisional application, Serial No. 244,510, filed February 6, 1905, as a continuation of the present application I have made claim to said water-heating means.

In my said Patent No. 461,429 the hot-water pipe (therein termed a "casing") by which the hot water is carried down into the mine opens at the bottom into the upper part of the cavity from the bottom of which the melted sulfur is removed; but in my apparatus, Patent No. 461,430, also dated October 20, 1891, it is shown also as being extended into the sulfur deposit and terminating a short distance above the lower end of the pipe up which the melted sulfur is raised. In both cases, however, the hot water is introduced at one place only and there is only one hot-water pipe. A feature of the present invention consists in delivering the hot water into the sulfur deposit at different levels—namely, at a short distance above the intake for the melted sulfur and at the upper part of the sulfur-bearing deposit. This double delivery of the hot water tends to counteract the bad effects of the water naturally present in the sulfur-bearing strata. This natural water being heavier than the hot water tends to flow in under the latter, mixing with it and cooling it if introduced in the lower part of the mine-cavity or if the hot water is introduced at the upper part of the cavity being liable to chill the melted sulfur. By the upper delivery a flow of the hot water over the walls of the cavity is secured, while the lower delivery prevents the chilling of the sulfur. A further feature in the same connection is the use of two hot-water pipes for the upper and lower deliveries, respectively, so that the amount at each delivery can be regulated from the top of the ground.

The invention also comprises such other parts, improvements, and combinations as are hereinafter set forth.

In the accompanying drawings, which form part of this specification, Figure 1 is a diagram illustrating sulfur-mining apparatus invented also by me which can most advantageously be employed in carrying out the present invention. Fig. 2 is a detail view showing the lower part of the air-injecting pipe, the sulfur-raising pipe, and one hot-water pipe; and Fig. 3 is a detail view showing the interior construction of the hot-water heaters.

In installing the mine apparatus the pipe A is driven down to the rock, and a hole is then drilled into the same. If on account of the porosity of the rock it is either too weak to furnish a proper foundation for the pipe A or would let much of the hot water escape to waste, a hole is drilled for a predetermined distance and the so-made cavity is filled with a mixture, more or less fluid, of cement and water, which mixture is subjected to pressure to force it into the rock. The hole may be of the same diameter as the interior of the driven pipe A, although this particular diameter is not essential. Portland cement is recommended for the mixture. Pressure may be applied to the cement mixture as or after it is run in by compressed air or other medium to the extent of, say, three hundred pounds, or more or less, as may be thought best. After the cement has hardened a hole is then drilled through the artificial rock B, and so continued (with or without the further formation of artificial rock) to and through the sulfur-bearing deposit C. When the well-hole is ready, the inner hot-water pipe D, the sulfur-raising pipe E, and the air-injecting pipe F are inserted. The hot-water pipe D, as shown, has a plug D′ with a perforation therein, through which the sulfur-raising pipe E passes. On said plug D′ the collar E′ of said pipe E rests. The lower end of the pipe E, as shown, opens into a strainer D″, formed by an extension of the pipe D. The wall of the pipe D just above the plug D′ is perforated for the escape of the hot water into the mine. The wall of strainer D″ is perforated, so as to let in the melted sulfur, but to keep out any solid particles. Should the holes in the strainer become clogged, the pipe E, with its collar E′, can be lifted and hot water be forced through the plug D′ into the strainer D″ and out through the perforations in the wall thereof. The air-injecting pipe F, as shown, extends nearly to the bottom of the pipe E and is provided at its lower end with a perforated piece F′, of zinc or other metal non-corrodible by sulfur—as aluminium, for example. These perforations are best made small, (say one-sixteenth of an inch in diameter,) so as to mingle the air in small bubbles with the melted sulfur. The sulfur-raising pipe E and other parts of the apparatus (as the air-pipe F and strainer D″, with the lower portion of the pipe D, for example) which are exposed to the melted sulfur are best made of galvanized iron or steel, the coating of non-corrodible zinc protecting the corrodible iron surfaces from the melted sulfur. The joints may with advantage be further protected by a coat of white lead ground in linseed-oil.

The pipes A and D are supplied with hot water, (it might be from any suitable source, but most advantageously from the heaters G H J.) These would ordinarily be jacketed to retain the heat therein. They consist each of an elongated upright tank having a steam-inlet pipe 2 from a generator, (not shown,) a water-inlet pipe 3 from a pump, (not shown,) a hot-water and steam outlet pipe 4, and appliances within the tank for securing an intimate commingling of the steam from the pipe 2 with the water from the pipe 3. The heaters may be supplied all from the same generator and the same water-supply pump, or there may be different steam-generators and water-supply pumps (either or both) for the different heaters. The pipes 4 conduct the hot water and steam from the heaters to the hot-water pipes A and D, which become filled to a certain height with the hot water and above this hold steam under pressure. At 5 and 6 valves are shown for closing the inlets to pipes A and D whenever such closure may be necessary or desirable.

As shown in Fig. 3, the steam-and-water-mixing appliances within the heaters G H J consist of a stack of pans K, of which only a portion is shown. Practically a stack of seventy pans of twenty inches in diameter is recommended as suitable for heating one hundred and twenty-five gallons of water per minute, the tank of the heater being supplied with live steam under a pressure of ninety pounds to the square inch above atmospheric pressure. The temperature of the steam would consequently be about 335° Fahrenheit, as is known. The pans are best made of cast-iron three-quarters of an inch thick, although other materials and other thicknesses may be used. It is considered an improvement, however, to employ a mass of metal largely in excess of that of the water and steam present at any one time in the tank, so that such metal may act as a regulator in taking up and giving out heat derived from the steam. The number and size of the pans can of course be varied, so long as a sufficient admixture is secured. The pans are set one upon another and are held apart by the legs 7, by which they are supported. In the bottom of each pan are perforations 8, surrounded by low rims, so that each pan will contain a layer of water, with a steam-space between it and the under side of the pan above. The bottom pan preferably rests upon a frame 7*.

The water-inlet pipe 3 is sealed at the inner end by the cup 9, and at the bottom of the tank there is a water-gage 10. This should not be allowed to contain water unless it is desired to have in the sulfur deposit a pressure equal to a water column the full depth of the mine plus the steam-pressure in the heater.

The operation is as follows: Water (at, say, the ordinary temperature) is pumped into the heaters through the pipes 3 and high-pressure steam is let in at the pipes 2. The water fills the pans to the tops of the rims around the perforations 8, through which it descends from pan to pan, being thus showered repeatedly through the high-pressure steam and exposed thereto in layers. The pans also act as conductors in conveying heat from the steam to the water. The volume of water and the volume, pressure, and temperature of the steam are adjusted to yield a proper supply of hot water for the fusion of sulfur in the mine. With the figures hereinbefore given the water should have on leaving the heaters G H J approximately the temperature of the steam—namely, about 335° Fahrenheit—with steam of about ninety pounds pressure. This temperature is considerably above that at which melted sulfur begins to darken. This is a desirable mode of working; but steam of a higher pressure than corresponds approximately with the temperature desired for the water to be pumped into the mine could be used, a less intimate mingling of steam and water being employed. Ordinarily the steam and hot water flow together through the pipes 4 to the mine-pipes A and D, which the water fills to a certain height, leaving the space above to be occupied with steam. This is a desirable condition, as the steam warms the pipes, and there is consequently no diminution in the temperature of the water until it descends below such underground steam-space. The water from the pipe A, which is preferably the larger in amount, flows around the walls of the mine-cavity and fuses the sulfur in said walls, which sulfur flows to the bottom of said cavity and forms a pool around the strainer D″ and lower end of the sulfur-raising pipe E. The water from the pipe D flows over the top of the melted sulfur and serves mainly to keep it and the contents generally of the mine-cavity at a high temperature. This mine-cavity is the deposit from which the sulfur has been melted out, and it of course holds water in the place of sulfur so removed; but it may hold also the rock in which the sulfur was embedded. The hot water is forced out through the walls of the mine-cavity and flows away through the surrounding rock. By reason of its high initial temperature it can travel farther from the sulfur-pipe before its temperature falls below the melting-point of sulfur, and even after its temperature has fallen below the melting-point of sulfur it imparts heat to the rock in the vicinity of the mine-cavity, and so aids in keeping the water in the said cavity at the sulfur-melting temperature. The melted sulfur settles by gravity in a pool about the lower ends of the pipes D and E, sealing the pipe E against admission of water thereinto. The melted sulfur is forced by the pressure in the mine-cavity up into the sulfur-raising pipe E. If a sufficient pressure is available, it can be thereby forced in a solid column aboveground; but where such pressure is not available it is most advantageous to reduce the average density of the column in the pipe E by injecting air through the pipe F into the melted sulfur near the base of the column. This air when it enters the pipe F may have the temperature of the melted sulfur or even a higher temperature, it being most conveniently allowed to retain heat imparted to it in the act of compression. The air may be injected in sufficient amount to constitute half the volume of the column, so that the average density of the melted sulfur mingled with air is about the same as that of water, and it may be used in even larger volume. Of course when a less average density is desired the amount of air may be proportionately reduced. Practically the amount of air is adjusted to the available pressure in the mine, and the air is compressed to such degree as to induce the flow of about the desired amount into the melted sulfur through the fine perforations at the lower end of the pipe F. The mingled air and sulfur are delivered from the pipe E into vats, in which the sulfur collects, the air leaving the sulfur while the latter is still liquid. As the sulfur is delivered without water, (the little which may accompany the sulfur being insufficient by its vaporization to solidify the melted sulfur,) it may be discharged at atmospheric pressure.

Instead of air other aeriform fluid may be used, as superheated steam, ordinary high-pressure steam, carbonic acid, or other inert gas, or even a volatile liquid, (like water,) which may assume the aeriform state as it is (or after it has been) injected into the melted sulfur.

In my divisional application, Serial No. 182,359, filed November 23, 1903, as a continuation of the present application, I have claimed mining apparatus herein shown, and I have made this division of my claims (for apparatus and for process, respectively,) solely in consequence of official requirement. In my application, Serial No. 244,508, filed February 6, 1905, as a continuation of the present application in so far as it discloses matter herein disclosed, I have claimed the installation of a well by the aid of a foundation of artificial rock for the casing and have included in my claims both the installing process and the well itself. The making in said application of claim to matter herein disclosed is solely in consequence of official requirement of division, although I have also included additional improvements in the installation of wells in said application.

I claim as my invention or discovery—

1. In sulfur-mining in porous rock, the improvement consisting in forcing hot water into the underground deposit and out through the walls of the mine-cavity, so that it flows away through the surrounding rock, and removing the melted sulfur which separates itself by gravity from the water in the mine, substantially as described.

2. In sulfur-mining in porous rock, the improvement consisting in forcing water heated above the temperature at which melted sulfur begins to darken into the underground deposit and out through the walls of the mine-cavity, so that it flows away through the surrounding rock, and removing the melted sulfur which separates itself by gravity from the water in the mine, substantially as described.

3. As an improvement in sulfur-mining, and in conjunction with the fusion of the sulfur in the underground deposit, the introduction into a column of the melted sulfur of air or other aeriform fluid, so as to form a column of melted sulfur of diminished density to be raised by pressure in said deposit, substantially as described.

4. As an improvement in sulfur-mining, and in conjunction with the fusion of the sulfur in the underground deposit, the introduction into a column of the melted sulfur of air or other aeriform fluid in sufficient volume to form a column of melted sulfur of an average density approximating or even falling below that of water, substantially as described.

5. The method of removing sulfur from porous deposits wherein the natural pressure is less than that of the column of melted sulfur to be lifted, by fusing the sulfur in such deposit by hot fluid under such inferior pressure, and introducing air or other aeriform fluid into the column of melted sulfur so that this latter is lifted by the available pressure, substantially as described.

6. In sulfur-mining in porous rock, the improvement consisting in forcing hot water into the underground deposit and out through the walls of the mine-cavity, so that it flows away through the surrounding rock, allowing the melted sulfur which separates itself by gravity from the water in the mine to collect until it seals the end of the sulfur-pipe, and introducing air or other aeriform fluid into the column of melted sulfur so as to reduce its density and allow it to be raised by the pressure in the mine-cavity, substantially as described.

7. In sulfur-mining, the improvement consisting in bringing water for fusing the sulfur into contact with high-pressure steam in such manner as to effect the condensation of the latter, and conducting the first-mentioned water along with the water of condensation into the underground deposit, substantially as described.

8. In sulfur-mining, the improvement consisting in bringing water for fusing the sulfur into contact with steam of such pressure and in such manner as to effect the condensation of the latter and a heating of the water above the temperature at which melted sulfur begins to darken, and conducting the first-mentioned water along with the water of condensation into the underground deposit, substantially as described.

9. As an improvement in sulfur-mining, the passage of water for fusing the sulfur through a heater wherein it is brought in contact with high-pressure steam, and thence conducting it together with the additional water from the condensation of the steam to the underground sulfur deposit, the water in said deposit being constantly subjected to the steam-pressure, substantially as described.

10. As an improvement in sulfur-mining the passage of water for fusing the sulfur through a heater wherein it is brought in contact with high-pressure steam, and thence conducting it together with the additional water from the condensation of the steam to the underground sulfur deposit, uncondensed aeriform steam being conveyed underground to a greater or less distance, and the water in said deposit being constantly subjected to the steam-pressure, substantially as described.

11. As an improvement in sulfur-mining the passage of water for fusing the sulfur through a heater wherein it is brought in contact with high-pressure steam in such proportion and with such intimacy of contact, as by subdivision of the water into numerous layers and showerings in an atmosphere of said steam, that the temperature of the water is raised by the steam approximately to the temperature of the latter, and thence conducting to the underground sulfur deposit

under the pressure of said steam the so-heated water together with the water of condensation derived from the steam, substantially as described.

12. As an improvement in sulfur-mining by fusion underground, in conjunction with the removal of the melted sulfur, the introduction concurrently with said removal of the hot water for fusion into the underground sulfur deposit above and in proximity to the intake for the melted sulfur and also at a higher level near the upper part of the mine-cavity, substantially as described.

13. The method of removing sulfur from porous deposits wherein the natural pressure is less than that of the column of melted sulfur to be lifted, by fusing the sulfur in such deposit by hot water under such inferior pressure, and introducing air or other aeriform fluid into the column of melted sulfur so that this latter is lifted by the available pressure, substantially as described.

14. The method of mining sulfur, by fusing the sulfur in the mine, introducing air or other aeriform fluid into a column of the melted sulfur, raising the so-formed column of melted sulfur and air by the aid of pressure in the mine, and allowing the air to escape from the so-raised sulfur while this is still liquid, substantially as described.

15. The method of mining sulfur, by forcing into an underground sulfur deposit a hot fluid, such as water at a temperature above the fusion-point of sulfur and under a pressure less than that of a column of melted sulfur equal to the depth of said deposit below the level of the ground, so as by said fluid to fuse the sulfur in the deposit and establish a column of melted sulfur part way to the level of the ground, and introducing air or other aeriform fluid into said column for enabling said pressure to raise the sulfur all the way, substantially as described.

16. As an improvement in mining sulfur, and in conjunction with the forcing of hot water into an underground sulfur deposit to fuse the sulfur therein and establish a column of melted sulfur, the introduction of heated air into the said column of melted sulfur for enabling the melted sulfur to be raised to the level of the ground, substantially as described.

17. In mining by the aid of hot water introduced under pressure into an underground deposit from which the material to be mined is removed in a liquefied state, the improvement consisting in forcing the water into and mingling it with a body of high-pressure steam, and introducing the so-heated water without losing its pressure into such a deposit, substantially as described.

18. In mining by water, the improvement consisting in subjecting the water in an underground deposit to the joint pressure of a water column above the deposit and a body of compressed aeriform fluid above the water column, substantially as described.

19. In mining by fusion in porous rock, the improvement consisting in melting the material being mined in the underground deposit by means of fusion fluid introduced thereinto, which fluid is forced out through the walls of the mine-cavity into the rock beyond, and removing the melted material, substantially as described.

20. In mining by fusion, the improvement consisting in melting the material being mined in the underground deposit by means of fusion fluid introduced thereinto, and removing the melted material by the pressure in the deposit aided by the presence of aeriform fluid in regulable quantity in the column containing the melted material which is being removed, substantially as described.

21. In mining by fusion, the improvement consisting in introducing fusing fluid into an underground deposit near the top and bottom of the mine-cavity contemporaneously, substantially as described.

22. In mining by fusion, the improvement consisting in introducing fusing fluid into an underground deposit near the top and bottom of the mine-cavity contemporaneously and forcing the said fluid out through the walls of said mine-cavity into the rock beyond, substantially as described.

23. In mining by fusion in porous rock, the improvement consisting in melting the material being mined in the underground deposit by means of fusion fluid introduced thereinto, which fluid is forced out through the walls of the mine-cavity into the rock beyond, and removing the melted material by the pressure in the deposit aided by the presence of aeriform fluid in regulable quantity in the column containing the melted material which is being removed, substantially as described.

In testimony whereof I affix my signature in presence of two witnesses.

HERMAN FRASCH.

Witnesses:
T. W. LOTHMAN,
J. C. UPDEGROVE.