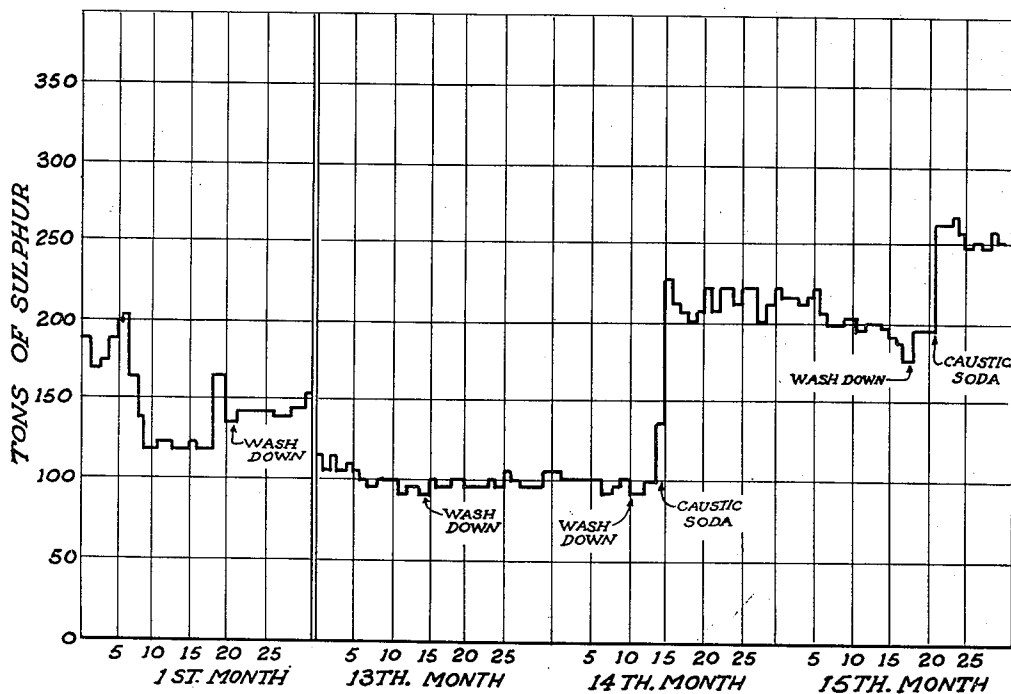


Nov. 20, 1956

J. E. MONROE, JR
PROCESS FOR REMOVAL OF DEPOSITS FROM SULFUR MINING
PIPES USING HOT CAUSTIC SODA SOLUTION
Filed April 6, 1953

2,771,284

DAILY PRODUCTION FROM TEST WELL



INVENTOR.

John E. Monroe Jr.

BY

Pollard & Johnston
ATTORNEYS

1

2,771,284

PROCESS FOR REMOVAL OF DEPOSITS FROM SULFUR MINING PIPES USING HOT CAUSTIC SODA SOLUTION

John E. Monroe, Jr., Port Sulphur, La., assignor to Freeport Sulphur Company, New York, N. Y., a corporation of Delaware

Application April 6, 1953, Serial No. 346,968

6 Claims. (Cl. 262—3)

This invention relates to the mining of sulphur and is concerned more particularly with procedures for the removal of obstructive deposits which after a time accumulate in sulfur conveying pipes and in bleedwater pipes employed in bringing sulfur or bleedwater from the formation at the bottom of the well to the surface. The sulfur pumping rate is thereby increased or restored to its original volume of flow.

It has been known for a long time in the mining of sulfur by the Frasch process using a concentric pipe system that there comes a time in the operation of the mines that the sulfur cannot be pumped out of the mine as fast as it is melted at the bottom of the well. This condition has, in the past, been attributed to the plugging of the sulfur inlet holes around the end of the sulfur conveying pipe or sulfur line at the bottom of the well by sand or pieces of formation rock which naturally would impede the flow of sulfur into the pipe. The reduction in pumping rate is now known to be caused in part by the formation of scale, of the character hereinafter described, in the well equipment and in the sulfur line both in the lower sections in the bottom of the well and in the upper sections near the surface.

When reduction of pumping rate of sulfur mines has been attributed to plugging, it has been the conventional procedure to force substantial amounts of hot water at the normal temperature used in mining, as 325–350° F. down into the sulfur formation at the bottom of the well both through the outside eight inch concentric pipe (the water pipe or line) and through the inner four inch pipe (the sulfur pipe or line). Usually this operation is successful in partially restoring the sulfur pumping rate when mining is resumed, but the increased rate cannot be maintained and the cleaning treatment must be repeated every few weeks and at decreasing intervals.

As far as is known, no other practical method has been successfully employed for removing the obstructive materials causing the reduction in pumping rate. Replacement of pipes on which the deposits occur is possible but too costly.

In wells where the sulfur-bearing strata contains a relatively high content of crude oil, the rate of diminution of sulfur pumping is relatively high and investigation has now revealed that it is caused by formation of deposits composed of various mixtures of inorganic substances as sulfides and oxides of iron and calcium carbonate, together with carbon, various carbon-sulfur complexes, as tars and asphaltic materials and occluded elemental sulfur which will not melt at mining temperatures. Since these substances are insoluble in water, the back washing treatment hereinbefore described can be only partly effective. Hence much or most of the deposit is not removed. For some reason the slight benefit of the washing that is obtained persists only for a short while. Even when the innermost 1¼ inch concentric pipe (the compressed air line) which is encrusted on its exterior wall is replaced with a clean one, the benefit is soon lost.

2

The primary object of the invention is to provide a process capable of restoring sulfur mines to the original or high sulfur pumping rate when reduction in this rate has been caused by the deposition of scale or other obstruction in the sulfur mine. A specific object is to provide a practical process for the removal of obstructive deposits which accumulate within the sulfur lines in sulfur mines.

In accordance with the process of the present invention, the obstructive deposits in the mine are removed and the sulphur pumping rate restored by subjecting the deposits to the action of caustic soda under conditions and for a time which loosens and removes the same, after which the solution containing the deposit is flowed out of the pipes.

The action of the caustic in loosening and removing the deposits is not fully understood, but it appears that it reacts with or dissolves that part of the deposits acting as bonding agents for the other components which are insoluble in the solution and that when the caustic is subsequently flowed from the pipes the solution takes with it the soluble components in solution and the insoluble components in temporary suspension. The caustic appears to dissolve or react with some of the carbon-sulphur complexes, the tars and asphaltic materials and with the hardened or frozen sulphur. The carbon, the inorganic materials and other carbon-sulphur complexes come off in the form of particles of various sizes and shapes after being released by dissolution of the bonding material.

In accordance with a preferred embodiment of the invention, the action of the caustic soda solution upon the deposits within the sulfur-conveying pipe is aided by heat. Hot water at the temperatures used in the mining of sulfur as from 310° to 365° F. is pumped down the surrounding water line into the formation, the sulfur line and the air line being closed off at their top ends. The hot water in the surrounding pipe heats the caustic soda solution to its boiling point at atmospheric pressure or to a higher temperature. The action of the caustic soda solution in reacting with or dissolving the frozen sulfur and the intermediate sulfur-carbon complexes is facilitated and increased by the action of the heat, and as a result, the deposits are more completely loosened and removed and the operation is made effective in a shorter period of time.

Although the caustic soda solution may be introduced into the sulfur-conveying pipe either in hot or cold condition, it is introduced in a hot condition, in a specific embodiment of the invention, the heat being derived from the heat of solution resulting from the admixture of caustic soda flakes with water immediately before the solution is pumped into the sulfur mine. The heat of solution will provide a solution at 140° F. or higher.

The concentration of the caustic solution may be varied within wide limits. There is no upper limit in concentration, for highly concentrated and saturated solutions effectively remove the deposits. When a concentration lower than about five percent is employed the effectiveness of the solution decreases and utilization of such weak solutions is not practical. Solutions of from 10–25% are preferred.

Since the action of the caustic soda upon the deposits is a time reaction the solution must be kept in contact with the deposits for an adequate period of time and when a 20% caustic solution is employed one or more treatments of a total time of one hour is usually sufficient. A series of treatments of one-half hour can be employed and such procedure may be preferred where excessive amounts of heavy solids are present in the deposit to be removed.

In operation of the process danger is involved in the settling out of the loosened scale in the bottom of the sulfur line, thereby plugging the perforations in the pipe at the bottom thereof. In accordance with the preferred operation of the process, the caustic soda solution together with the dissolved bonding material and solid particles are forced out of the well at the surface through the introduction of compressed air part way down into the mine as is done in conventional mining practice for assisting the flow of sulphur to the surface, while simultaneously hot water is pumped down the water pipe to keep the sulphur in a molten condition.

If the amount of insoluble scale in the deposits removed by the caustic solution is relatively small, the used caustic solution containing the dissolved deposit may be forced, upon completion of the chemical action, down and out of the bottom end of the sulfur pipe into the formation. This procedure, however, may cause plugging and hence is not preferred.

The speed of action and the effectiveness of the caustic soda treatment can be facilitated by a preliminary treatment involving the step of forcing hot water down the sulfur-conveying pipe into the formation, as is now done in efforts to restore higher sulfur pumping rates. Some molten sulfur or meltable sulfur adheres to the deposits on the interior walls of the sulfur pipe and on the opposed outside surfaces of the air line and the introduction of hot water over these surfaces melts away this sulfur and thus lessens the amount of sulfur to be dissolved by or reacted with the caustic soda solution in the treatment to follow.

In accordance with a specific embodiment of the invention, the process is applied to the cleaning of bleedwells, these wells being those from which formation water flows or is pumped in a volume approximately equal to the volume of mining water used, in order to keep the formation pressure constant. If the volume of flow decreases from these wells, it is customary that the flow be assisted by means of compressed air in the same manner that the flow of sulfur is assisted under the airlift principle. It has been determined that the decrease in flow up the bleedwell lines is frequently due to the deposition of sulfur, calcium carbonate and ferrous sulfate on the inside of the pipe, and when air is used to assist the bleeding operation, oxidation of hydrogen sulfide to elemental sulfur is increased thereby decreasing the flow rate rapidly in spite of the airlift.

In removing the deposit from the bleedpipe, the caustic soda solution may be pumped into the pipe and permitted to remain until the deposit has been dissolved and loosened, after which the caustic solution and contained deposit may be forced to the surface and discharged to waste upon resumption of the bleeding step in connection with the sulfur mining operation. Any concentration of caustic above about five percent can be used, but in any specific operation, the solution must not be so heavy that it will overbalance the bleedwater column and thus flow down into the formation.

Alternatively the bleedpipe may be cleaned by circulating the caustic soda solution down the air line and up the bleedliner or water-conveying pipe to the surface. Since the deposition and clogging of the bleedpipe appears to occur more profusely in the annulus between the air line and the water line, a combination treatment is preferred in which this portion of the pipe is given a more severe treatment with the caustic soda solution than the lower section. This result is accomplished by continuously circulating the caustic soda solution down the air line and up the bleedline for a period of an hour or more and then introducing additional caustic soda solution into the section of the bleedline below the bottom end of the air line and leaving this solution in contact with the pipe for one-half hour to one hour or more until dissolution of the deposit has occurred.

Example 1

The sulfur well is first washed with conventional hot water by forcing the same downwardly through the sulfur-conveying line for a period of twenty minutes. This treatment melts and removes the free sulfur from the surfaces of the deposits within said pipe and it also forces sand and broken pieces of formation rock from the perforations in the bottom of the sulfur line. Next four hundred gallons of freshly prepared, hot, caustic soda solution of 20% strength is pumped down into the sulfur pipe thereby filling the same. Hot water at a temperature of 325° F. is also pumped down into the well in the surrounding water line. This water not only prevents any solidification of sulfur in the well but it also maintains the caustic soda solution at a high temperature, at least as high as that of molten sulfur, namely 238° F.

The hot caustic soda solution is permitted to stay in the well for a period of one hour. Thereupon the surface discharge end of the sulfur-conveying pipe is opened and the flow of water down the water-conveying pipe continues while the caustic soda solution containing the dissolved deposit and loosened scale flows up the sulfur line toward the surface. Compressed air is forced down the air-line in conventional manner and as a result the caustic soda containing the removed deposits flows from the well to the surface and to waste. When the caustic solution is removed from the well, which fact is determined by the presence of molten sulfur in the effluent stream, the well is shut down and the sulfur pipe is again washed down with hot water for approximately an hour in order to remove any dislodged scale particles which have accumulated around the perforations in the bottom of such pipe. The well is then returned to service.

The results obtained by the practice of the present invention substantially in accordance with the procedure described in the foregoing example is illustrated in the accompanying drawing setting forth the daily production of sulfur from a well which had been producing around one hundred and fifty tons per day for some months and around one hundred tons per day for the several next preceding months. It will be noticed that the wash down treatments had very little effect in restoring flow whereas the caustic soda treatment had a very marked effect in both instances in increasing the rate of flow, i. e., to about two hundred and later to about two hundred and fifty tons per day.

Example 2

The bleedwell subjected to the process of the present invention bled initially at an average rate of 200 G. P. M. at a formation pressure of 30 p. s. i. and after a period of four months, a volume varying between only 100 to 150 G. P. M. was obtained, the flow at this time being assisted by the introduction of compressed air. This low volume had continued for several months when the process of the present invention was applied to the bleedwell.

Four hundred pounds of caustic soda flakes were mixed with sufficient water to yield four hundred gallons of solution or a 10% concentration by weight. A wellhead or formation pressure of 20 p. s. i. was obtained by shutting off the compressed air introduced into the bleedwell and allowing the well to bleed back through the air line.

The caustic soda solution at a temperature of about 140° F. was pumped down the air line into the well and the bleedliner was allowed to bleed at the surface at a rate estimated to be equal to the injection rate.

When the return flow began increasing in gravity showing that the caustic soda solution was reaching the surface, the discharge from such pipe was collected and pumped again down the air line. The input and output volumes were kept equal during the recirculation and enough fresh water was added to the recirculating solution to hold the gravity below 1.09. The recirculation of the solution was continued for a period of one hour and

during this time the effluent solution took on a very dark amber color and it contained a large amount of material in suspension. Upon cessation of the circulation the discharge outlet from the liner was closed and the solution remaining in the circulating tank at the surface was forced down into the bleedwell into the section below the bottom end of the air line. Thereupon another four hundred gallon batch of fresh 10% caustic soda solution was pumped down into the well in the same manner. The solution was permitted to remain in the well for a period of about forty-five minutes.

After the surface bleedline was reconnected to the well, compressed air was injected through the air line and caustic solution in the liner was forced to the surface. Upon resumption of normal operation of the bleedwell, large amounts of sulfur and other scale were brought to the surface and flowed into the bleedwater pit. After about four hours the amount of sulfur and scale decreased but the flow remained somewhat cloudy for sixteen hours thereafter. The flow of bleedwater assisted by the compressed air was roughly four hundred G. P. M. and when the air was cut out of the well some hours later, a steady flow of two hundred G. P. M. at 30 p. s. i. formation pressure was obtained thereby showing that the deposit had been substantially completely removed.

In the foregoing bleedwell cleaning process, the caustic soda solution of 10% concentration was used to ensure satisfactory operation. A check on the density of the bleedwater normally coming from the mine revealed a specific gravity of 1.0002. The 20 p. s. i. closed-in pressure recorded at the wellhead was calculated to allow an increase in gravity of the fluid in the space between the air line and the bleedwater line in the five hundred foot length to 1.092 before circulation would cease. This gravity correspond roughly to that of a 10% solution of caustic soda at 60° F. As a safety feature against loss of circulation, the specific gravity of the caustic soda solution to be used was based on 60° F. while making no allowance for decrease in gravity which results from the increased temperature caused by the heat of solution of the caustic.

The process of the invention has several outstanding advantages as follows:

1. The process very satisfactorily increases the sulfur pumping rate of the mine and improved rates have been obtained in every instance in which it has been employed.
2. The gain in pumping rate of the mine has continued over a sufficient period of time to indicate that the effect is one of considerable duration.
3. The process can be conveniently practiced with little or no extra equipment and no outside service is required.
4. The period of interruption in sulfur production caused by operation of the process is small enough to be of little consequence.
5. The process may be operated at a comparatively low total cost and appears to be the best means yet devised for removing scale.

Although economic considerations may require the use of caustic soda as the reactant used in the process of the present invention, it should be understood that equivalent caustic compounds may be employed, that is other alkali metal hydroxides.

It should be understood that the present invention is not limited to the details herein given as to materials and procedures used or to the exact conditions employed, for it extends to all equivalents which will occur to those experienced in the art upon consideration of the terms employed in the claims appended hereto.

I claim:

1. In connection with the mining of sulfur by the Frasch process using a concentric pipe system, a process for removing obstructive deposits accumulated within the sulfur conveying pipe, containing carbon-sulfur complexes and inorganic material which comprises flowing

hot caustic soda solution down into said pipe, subjecting the deposit to the action of said hot caustic soda solution until such removal has occurred and during such action heating the pipes on which the deposit occurs by flowing hot water down the surrounding water conveying pipe and flowing the used caustic solution together with the removed deposit from the pipe up to the surface by means of water and of compressed air introduced through an air pipe down into said pipe containing the removed deposit.

2. In connection with the mining of sulfur by the Frasch process using a concentric pipe system, a process for removing obstructive deposits accumulated within the sulfur conveying pipe which comprises washing molten sulfur from the surfaces of the deposits by flowing hot water through the sulfur conveying pipe, filling the pipes containing the deposit with caustic soda solution, and after such deposit has been loosened, forcing the solution containing the loosened deposit from the system by means of hot water and compressed air introduced down into the system, whereby sulfur is melted and in rising to the surface forces the solution to the surface.

3. In connection with the mining of sulfur by the Frasch process using a concentric pipe system of at least three pipes, a process for removing obstructive deposits accumulated within the sulfur conveying pipe which comprises washing molten sulfur from the surfaces of the deposits by flowing hot water through the sulfur conveying pipe, filling the pipes containing the deposit with caustic soda solution, and after such deposit has been loosened, forcing the solution containing the loosened deposit from the system by means of hot water flowed downwardly in the outermost concentric pipe and compressed air forced down the innermost pipe.

4. In connection with the mining of sulfur by the Frasch process using a concentric pipe system, a process for removing obstructive sulfur-containing deposits accumulated within the pipes used which comprises flowing a caustic soda solution of at least five percent concentration down into the pipe containing such deposit, and after the deposit has been loosened from the pipe walls by the action of said solution, flowing the used caustic solution together with loosened material from the pipe up to the surface by means of water and of compressed air introduced through an air pipe down into said pipe containing the loosened deposit.

5. In connection with the mining of sulfur by the Frasch process using a concentric pipe system, a process for removing obstructive sulfur-containing deposits accumulated within the sulfur conveying pipe which comprises filling the pipes containing the deposit with caustic soda solution, and after such deposit has been loosened, forcing the solution containing the loosened deposit from the system by means of hot water and compressed air introduced down into the system, whereby sulfur is melted and in rising to the surface forces the solution to the surface.

6. In connection with the mining of sulfur by the Frasch process using a concentric pipe system of at least three pipes, a process for removing obstructive sulfur-containing deposits accumulated within the sulfur conveying pipes which comprises filling the pipes containing the deposit with caustic soda solution, and after such deposit has been loosened, forcing the solution containing the loosened deposit from the system by means of hot water flowed downwardly in the outermost concentric pipe and compressed air forced down the innermost pipe.

References Cited in the file of this patent

UNITED STATES PATENTS

1,049,054	Coombs	Dec. 31, 1912
1,382,337	Bellis	June 21, 1921