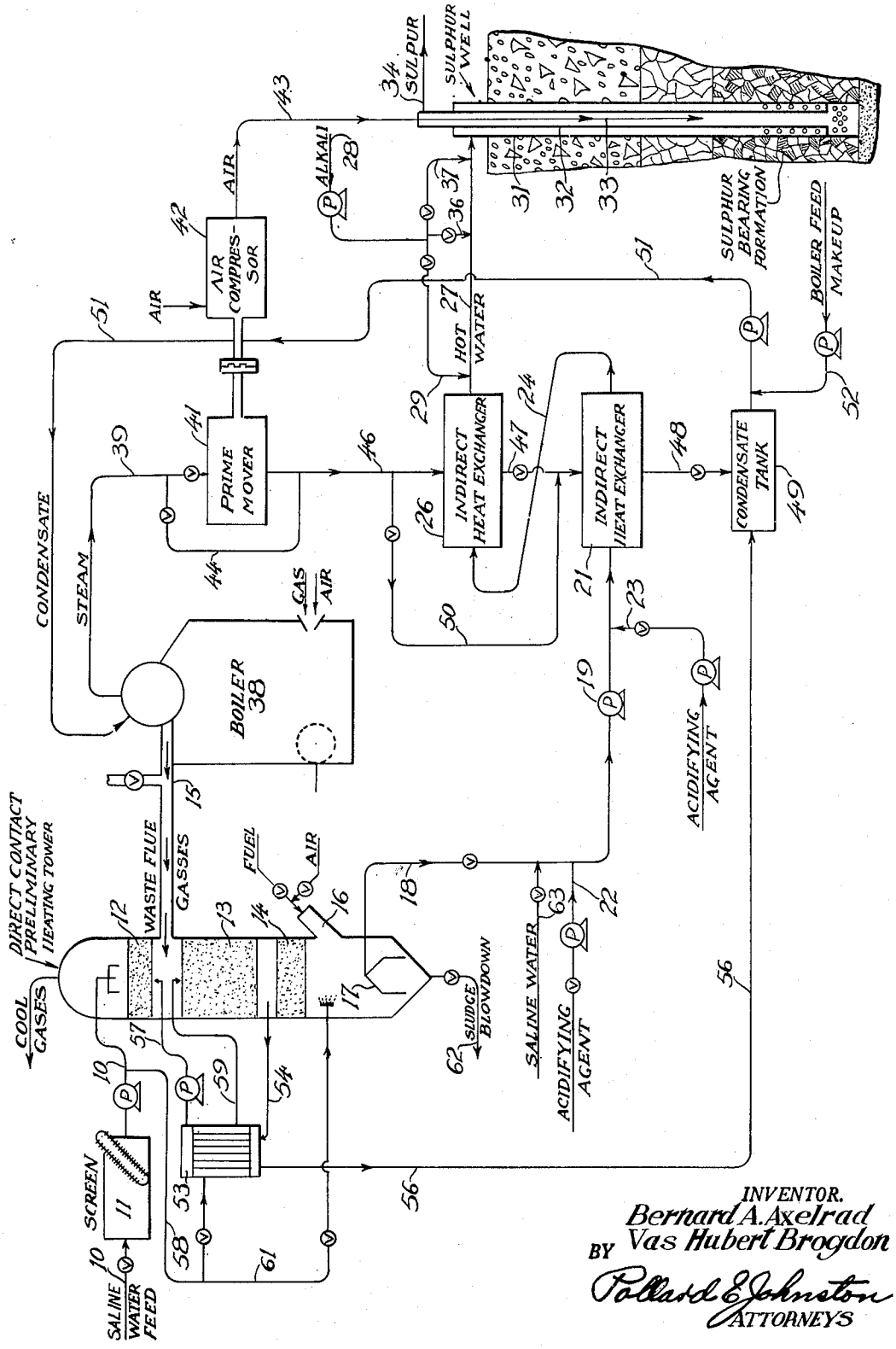
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HEATING OF SALINE WATER AND MINING OF SULFUR THEREWITH

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HEATING OF SALINE WATER AND MINING OF SULFUR THEREWITH

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This invention relates to a process for heating sea and other saline water of any salinity to high temperatures and more particularly to the heating of such waters to temperatures of at least 250° F. in indirect heat exchangers without causing the usual high rate of deposition of hard scale on the surfaces of the heating equipment.

The invention is also concerned with the mining of sulfur involving the utilization of super-heated sea and other saline waters for such mining operations.

If sea water is heated to high temperatures under ordinary indirect heat exchange practice, salts therein rapidly precipitate out and form a hard scale which reduces the heat transfer efficiency and soon requires that the equipment be taken out of use, opened up and scraped or turbined to remove the scale.

An ultimate object of the invention is to provide large quantities of very hot salt water at low cost. An intermediate object is to heat such water in indirect heat exchange equipment by a procedure which avoids a prohibitive rate of deposition of scale on the hot heating surfaces of the equipment.

A specific object of the invention is to cause scale-forming compounds including magnesium hydroxide and calcium carbonate which unavoidably separate out during the heating of salt waters of intermediate salinity to deposit for the most part in the form of a soft, non-adherent layer removable from the tubes simply by flashing or by flushing with steam or other fluid for a few minutes.

In the process of mining sulfur by the Frasch or underground fusion method, a hole is drilled into the sulfur bearing formation and the well equipped with a system of concentric pipes within a well casing. Super-heated water is pumped into the well and discharged into the formations through perforations in the outer pipe. The melted sulfur enters one of the inner pipes and is raised to the surface by a suitable means such as an air-lift. The mine water required for melting the sulfur is relatively large in volume in proportion to the sulfur removed, and is super-heated to a temperature generally in the range of 300–345° F. and forced into the formation under pressure.

The conventional sulfur mining plant requires a substantial supply of fresh water and considerable difficulties are experienced when the water available contains in excess of 50 grains per gallon of sodium chloride. By the conventional Frasch system of mining sulfur, at least 30 per cent of the water consumed is converted to steam and used in this form. This fact requires that at least 30 per cent of the water consumed be of acceptable quality for boiler-feed purposes. In a conventional plant, fresh water, taken from local streams during periods of fresh runoff and impounded in storage reservoirs, or well water is treated in efficient systems, usually of the hot process type, to minimize the scale deposition encountered when the water is heated. Because of the large volumes of water handled, accurate control of the treatment processes is required to minimize the restriction of water flow by scale deposition and also to minimize the down-time of equipment dismantled for cleaning.

Another requirement of the water heating process is that corrosion to heaters, pumps, pipe lines and other equipment be minimized and this is normally accomplished by reducing the hydrogen-ion concentration of the water used in the treating processes. Scale depositions, held to a minimum, offer some corrosion protection to the equipment. The heaters are normally vented to remove dissolved gases which contribute to corrosion. A substantial portion of the water consumed is treated to an acceptable quality for boiler feed purposes and is converted to steam. A major portion of the steam is used to heat the mine water to sulphur mining temperatures by direct contact. The water entering the sulphur bearing formations, therefore, consists of about 25 per cent steam condensed in the heaters. In addition, steam is utilized for production of electric power, compressed air and other processing needs.

The mine water is usually treated by a hot process lime system which reduces the temporary or carbonate hardness to a low value, but by virtue of the availability of fresh water, the non-carbonate or permanent hardness present is relatively low and need not necessarily be removed from the mine water. Water containing larger amounts of total solids, or water containing more than 200 grains per gallon of chlorides expressed as sodium chloride cannot be used as such following prior practices.

A principal object of the present invention is to provide processes for mining sulfur which successfully utilize sea and other saline waters containing total solids in amounts which prohibit the heating of the water to sulfur mining temperature levels in conventional equipment by reason of scale formations.

Another object of the invention is to provide a means of mining sulfur by processes requiring large volumes of superheated water from certain salt domes located in the Gulf Coastal marsh region and tidal areas where fresh water is not available. The existence of sulphur in commercial quantities in a number of these salt domes has been known for years, but the unavailability of fresh water and the distance through which fresh water would have to be transported has prevented the mining of these domes.

As is well known, sea water contains large amounts of calcium and magnesium salts which deposit from solution when the water is heated. The water in the bays near the salt domes in question appear to vary between 100 and 2000 grains per gallon of chlorides expressed as sodium chloride. The scale forming constituents are present in marsh and sea water in almost direct ratio to the chloride content.

Because of the very large quantities of scale forming constituents present in sea water or in marsh water of intermediate salinities, a chemical treatment for the complete softening of the water would be impractical. Because of the necessity of transporting fresh water for boiler feedwater make-up or of resorting to expensive processes for the production of satisfactory boiler feedwater from the salty water, such as distillation or complete chemical treatment, the instant invention utilizes a heating system of the indirect type providing for the return of the steam condensate to the boiler make-up system.

The hydrogen-ion concentration of the sea or marsh water cannot be decreased substantially without the deposition of calcium and manganesium salts and their deposition would be further accelerated in the heating process to an impractical extent. The prevention of corrosion in a sea or marsh water heating system is therefore a very serious problem, since the desired protection must be secured without benefit of a decrease in hydrogen-ion concentration.

In view of the difficulties referred to briefly above, the mining of sulphur from these salt domes in marsh areas

has long been regarded as impractical. A number of references to the presence of sulphur in these domes can be found in the literature with general statements to the effect that securing fresh water would be necessary for their operation. In the light of the continued increase in demand for sulphur and the evident eventual depletion of known deposits in more favorable locations, the invention is directed to the problem of developing a process whereby sea, marsh and other saline waters can be used in mining operations at these domes.

An immediate object of the invention is to heat sea and other saline waters for sulphur mining operations without including a prior treatment for the removal of dissolved solids, by a process which avoids excessive scale deposition in the water heating system and prevents corrosion of the equipment coming in contact with the saline water.

A further object is to provide a simple method for the separation of diatoms and other algae, salt and other colloidal matter from natural saline waters before such water is heated to sulfur mining temperatures in indirect heat exchangers.

A still further object is to provide a process for heating saline waters to sulfur mining temperatures which includes a treatment of the saline water after heating which will reduce its corrosion tendencies in relation to the pipes and auxiliary equipment conveying the heated water to and into the sulfur mines.

The copending application of the present applicants, Serial Number 244,854, filed September 1, 1951, now abandoned, describes an invention involving heating saline water containing the usual calcium sulfate and other scale-forming compounds to temperatures above 250° F. in a two stage indirect heat exchanger and controlling the heat transfer in the first stage such that scale-forming compounds in the water which separate out will deposit primarily or substantially only in the form of a soft, non-adherent layer in the first stage and controlling the heating in the second stage such that the thus obtained water can be and is heated to a higher temperature without causing deposition of appreciable amounts of hard scale on the heating surfaces of said stage.

In the two stage indirect heat exchanger of said process, the water is forced under superatmospheric pressure into the tube or bank of tubes constituting the first stage and is heated therein to a temperature at which scale-forming compounds in the water deposit substantially only as a soft, non-adherent layer by applying heat to the water from the heat exchange surfaces at a temperature predetermined to be below that at which the scale-forming compounds present in the water of the specific salinity treated will deposit as a hard adherent scale during the period the water is present in said stage. Next, the altered hot water thus obtained is flowed under the pressure through the tube or tubes of the second stage of the heat exchanger and therein heated to a higher temperature but below that predetermined to cause the calcium sulfate present to precipitate out in said stage during the period the water is present in said stage, by applying heat to the water from the heat exchanger surfaces maintained at temperatures predetermined to be below those at which calcium sulfate present in the altered hot water being heated will form a scale at a prohibitive rate during the period the water is present in said stage. Finally, the heated water is flowed from the said second stage before $CaSO_4$ precipitation has occurred. To maintain acceptable heat transfer rates in the tube or tubes, the soft layer deposited therein is periodically removed by forcing a fluid at high velocity through the tube.

The above described process is particularly effective in the heating of brackish waters or sea water of intermediate salinity, as those having from 600 to 1700 grams per gallon of total salts. The deposition of calcium sulfate scale from waters of any salinity is successfully prevented, but when waters of higher salinity are to be heated to the higher temperatures within the possible range, the said process

is less satisfactory, for part of the soft, non-sulfate deposit unavoidably changes to a hard scale under such conditions and the tubes must be turbined undesirably often.

A specific object of the present invention is to provide a process for heating sea water of high salinity, as sea water of 1700 G. P. G. salinity to high temperatures in indirect heat exchangers without encountering prohibitive hard scale formation on the heating surfaces of the tubes.

The process of the present invention in a contemplated embodiment includes the heating methods and the temperature controls of the said prior application but the instant invention includes an acidification treatment of the water before it is heated in the indirect heat exchanger which treatment ordinarily will make unnecessary the precipitation of part of the solids content in the form of a soft layer in the tubes of the first of the two heating stages.

It has now been discovered that the formation of the soft layer on the heating tubes can be greatly reduced and in some instances completely eliminated and that the conversion of any soft layer to hard scale can be lessened or completely prevented simply by increasing the hydrogen ion concentration of the saline water to be treated in accordance with the procedures hereinafter defined.

In its most important field of utility, the invention is concerned with the mining of the sulfur by the use of superheated saline water pumped down into the sulfur-bearing formation and the process involves a continuous operation which includes adding to a flowing stream of saline water a small amount of an acidifying agent, applying superatmospheric pressure to the water by means of a pump, conducting the treated water under pressure into and through an indirect heat exchanger preferably employing steam as the heating medium, heating the water in said exchanger to a sulfur-melting temperature required in the mining of sulfur as to 300° F. or more, maintaining the temperature of the heating surfaces in contact with the saline water below that predetermined to cause calcium sulfate present in the saline water to precipitate out and deposit during the heating operation, and pumping the resulting heated water while still under pressure into the sulfur-bearing formation. The sulfur is melted, collected and forced to the surface in accordance with usual practice.

Since the heated saline water leaving the heat exchanger is excessively corrosive due in part to the treatments previously applied thereto, it should be conveyed to and into the sulfur mine through surface lines and mine pipes protected on their exposed surfaces by a corrosion-resistant coating. The main lines carrying the heated water to the producing wells and, as well, the inside lining of the water conveying concentric pipes in the sulfur wells, may satisfactorily be composed of steel lined with Lumnite or other corrosion-resistant cement.

In accordance with a subordinate feature of the invention all of the exposed surfaces of such pipes including the outside of the sulfur-conveying concentric steel pipes in the sulfur wells are protected by the deposition of a limited, controlled amount of scale derived from the saline water itself by adding to the heated water leaving the heat exchanger a quantity of an alkali, preferably sodium carbonate or sodium hydroxide. The preferred treatment involves the addition of caustic soda in amounts within the range of 0.1 to 0.5 pound per 1000 gallons of water. Other precipitating or treating agents, such as barium chloride, sodium phosphates or sulphates, may be used. The amount added depends upon the salinity of the water, its temperature and extent of the acid pretreatment employed.

If the heated water is to be conveyed any substantial distance through surface lines, it is desirable in some cases that the alkali be added at more than one point between the heater and the mine, since it is most desirable that the scale be formed at a rate just sufficient to maintain a protective film on the metal surfaces. One

addition of alkali will usually be sufficient to form the desired coating in 2000 or more feet of the surface line. The treatment is controlled such that by intermittent deposition and solution or by deposition followed by maintaining proper chemical equilibrium in the water (so that scale will be neither deposited nor dissolved) a scale film is maintained which is sufficient to afford scale protection without excessive obstruction of the flow of water. Periodic examination of the condition of the scale deposition provides an easy method of determining the effectiveness of the alkali treatment and hence indicates adjustments of the amount, if required.

The invention may be utilized for heating any saline water, including sea water, marsh water, bay water, tidal water, river water and other like natural waters. It is useful for waters having a salinity greater than 50 G. P. G., but is especially useful for those having a salinity of at least about two hundred G. P. G. All of such waters invariably contain in addition to the sodium chloride, various scale-forming salts principally calcium sulfate, magnesium salts and calcium carbonate, and minor amounts of other compounds. Tests conducted in connection with such waters indicate that their hydrogen ion concentrations vary between 7.7 and 8.3 in pH value.

The acidification of the saline water, in accordance with the present invention is accomplished by the addition of an acidifying agent, either an acid or an acid-forming compound, the only limitation upon the nature of the acidifying agent added being that it is available and utilizable at an economically feasible price. Small amounts of mineral acids, as hydrochloric and sulfuric, or of acid-forming compounds as sulfur dioxide can be satisfactorily used. In accordance with a most important embodiment of the invention, carbon dioxide is added, either alone or in combination with a mineral acid.

The amount of the acidifying agent to be added for effecting optimum results can be preliminarily determined by utilization of the following discovery. When a sample of sea water is heated in a heat exchanger tube to a high temperature at which a soft layer (non-calcium sulfate) forms, the hydrogen ion concentration of the water is increased. For accomplishing the objects of the present invention an amount of acid or carbon dioxide is added to the water which alters its hydrogen ion concentration to a degree causing the same drop in pH which would occur in the heating process contemplated but in the absence of any acid pretreatment. The amount of acid or the extent of the acidic treatment required to prevent the deposition of hard non-sulfate scale can be calculated from the drop in alkalinity of a sample of the untreated water passed through a heat exchanger used in the laboratory in small scale tests which simulate the retention and method of heating used commercially.

It will be found that the minimum amount of acidifying agents required depends on the salinity or quality of the water being heated. Although the addition of any amount of acid is theoretically of some benefit, for practical advantage the amount should reduce the pH value to 7.5 or below. The preferred pH range is from 6.5 to 7.5 but at pH's below 6.5 the corrosion difficulties are increased.

When water of a salinity up to about 1500 G. P. G. is treated, the amount of acid to be added should be sufficient to reduce the pH value to 7.2 or below. When water of relatively high salinity is treated, it is preferable that the amount of acid be that which adjusts the pH to a value of 6.7 or below.

In operating under the simplest embodiment of the invention, a stream of hydrochloric or other mineral acid in a predetermined proportion is mixed with the stream of saline water to be heated, and the resulting water stream is then forced by means of a high pressure pump into the indirect heat exchanger.

In accordance with one hydrogen ion alteration embodiment of the invention, the saline water is preliminarily heated by direct contact with combustion or flue gases which contain carbon dioxide. The quantity of combustion gases required to heat the water is usually sufficient to provide the amount of carbon dioxide necessary to effect the increase in hydrogen ion concentration. The temperature of the gases and the heater are arranged to heat the water preferably to a temperature between about 140° and 195° F. The flue gases used may suitably be at temperatures of from 500° to the theoretical flame temperature for natural gas.

When operating under certain conditions, as at higher temperatures and higher salinities, it is preferred after applying superatmospheric pressure to the heated water, to make supplemental additions of carbon dioxide or a mineral acid, or both, in required amounts, whereupon the resulting treated water is conducted into the indirect heat exchanger under pressure.

Since the presence of oxygen dissolved in the water increases corrosion of the indirect heat exchanger tubes, the present invention contemplates employing specially produced combustion gases to accomplish the preliminary heating, which gases are produced from a burner or burners operated under controlled gas ratios to give a flue gas containing virtually no oxygen.

Under some circumstances it is desirable to insure the removal of the last traces of dissolved oxygen by adding to the preliminarily heated water a small amount of sodium sulphite, hydrazine or other suitable chemical. Removal of such oxygen may, in part, also be accomplished by passing the heated water through a vacuum deaerator, but such step removes part of the carbon dioxide. Special steps for the removal of oxygen may not be necessary when sulfur dioxide is used as the acidifying agent.

In a special embodiment of the invention the saline water is initially preheated in a packed tower or other suitable equipment by direct contact with flue gases from the boilers providing the steam for the indirect heat exchanger employed in the final step of the heating process of the invention. The heating with these gases may be used to advantage to heat the water to about 110° to 140° F. The thus heated water is then further heated in a second stage by combustion gases from auxiliary burners operating in the lower section of the same tower or in a separate tower or heat exchanger. The water in this stage is suitably raised to a temperature of about 180° to 195° F. These burner gases are preferably produced under the conditions hereinbefore described in order to avoid excessive corrosion tendencies in the indirect heat exchanger to which the preliminarily heated water flows. In order to minimize corrosion of metal surfaces of the resistant alloys used in the heater, the dissolved oxygen should be reduced to less than 0.3 part per million.

The preliminary direct heating is preferably carried out in a tower at atmospheric pressure in which the saline water is introduced at least in part at the top from which it flows downwardly over any suitable packing in contact with upwardly flowing combustion gases. During this heating the diatoms, silt and other colloidal matter are coagulated and settled out in any suitable manner and preferably in a pool formed in the bottom of the heating tower from which pool the water is decanted and the settled sludge periodically blown out.

For carrying out the main heating operation of the invention the preliminarily heated and purified saline water of adjusted hydrogen ion concentration is passed through a high pressure pump into the tubes of the indirect heat exchanger, the magnitude of the superatmospheric pressure applied to the water being sufficient to provide a pressure in the exchanger outlet greater than the vapor pressure of the water and preferably also above that of the dissolved gases. The initial pressure applied varies

with the ultimate temperature, the particular construction of the exchanger and other minor factors. Pressures of 250 to 350 p. s. i. are suitable minimums for operations primarily contemplated.

The maximum temperature to which the salt water may be heated in the indirect heat exchanger is determined to a large extent by the salinity of the salt water being heated. The greater the salinity of the water treated, the greater the amount of calcium sulfate present and the lower the maximum temperature possible. Heating to excessive ultimate temperatures leads to unavoidable precipitation and deposition of hard calcium sulfate scale. By limiting the ultimate temperature to a level below that at which the precipitation takes place from the hot water, such scale deposition can be substantially avoided.

The ultimate possible maximum temperature to which a water of any specific salinity can be successfully heated is influenced to some extent by the particular heat exchanger construction or system employed, the velocity of the water travelling through the tubes and the skin temperature of the heating surfaces. In actual operations, if salt water is desired at the maximum possible temperature, such temperature must be determined by trial and error in the specific exchanger to be used.

This limitation as to the ultimate possible maximum temperature is coupled with the requirements as to the manner of effecting the heating of the salt water in the heat exchanger tubes. If the deposition of hard scale in the tubes is to be avoided, not only must the ultimate temperature of the water be restricted, but also the skin temperature of the heating surfaces with which the water comes in contact. Heating of sea water to temperatures above 250° F. in heat exchangers in any number of steps (one or more), the utilization of conventional efficient heat exchange practice invariably leads to hard scale deposition.

In the instant process, the heating of the salt water in the indirect heat exchangers should be controlled in such manner that the skin temperature or temperatures of the heating surface with which the water comes in contact are always below the temperature predetermined to cause hard scale formation from water of the specific salinity treated during the period the water remains in the tubes.

During the continuance of the heating operation in the heat exchanger, it is necessary or desirable for efficient operation to alter the controls as the deposit eventually builds up in the tubes in order to maintain the desired final temperature constant.

Where steam at variable pressure is available, the preferred procedure involves maintaining a constant water velocity in the exchanger tubes and gradually increasing the steam pressure on the tubes of the respective heating steps to compensate for the reduction in heat transfer rate resulting from either the soft layer deposition or the scale formation. By increasing the steam pressure gradually, an excessive increase in the skin temperature of the water being heated is avoided. When the steam pressures on the tubes of the respective heating steps reach values previously established as the desired maximum from operating data, the heat exchanger tubes are cut out and flushed after which the steam pressure is reapplied at the initial minimum value and the process is resumed. The steam pressure in each step may be conveniently regulated automatically by suitable instruments to maintain the saline water leaving the respective heating step at a specified temperature.

Operation of several different heat exchangers in accordance with the present invention appears to indicate that the preferred velocity of the salt water in the heat exchangers is 5 to 9.5 feet per second, but velocities in the range of 4 to 12 feet per second could be used if the exchanger were designed consistent with the heat loads and temperature differentials present at the preferred range.

In an alternative system the steam pressure on the tubes of each step is maintained at a desired value and the water velocity in each individual tube is adjusted through certain limits and lessened to maintain the desired temperature of the salt water, and the flushing operation is carried out periodically to restore initial heat transfer rates. In this mode of operation the water volume is gradually reduced as the deposit forms thereby holding the water temperature substantially constant. Since the preferred apparatus involves a number of parallel streams of water passing through individual exchanger tubes, the regulation of the total water load on the plant can be accomplished in such a way that the combined water output is not materially changed.

Since the heating process of the instant invention depends upon the water velocity, temperature and temperature gradients, the invention contemplates in its broadest scope, systems of regulation other than those set forth above including combinations of the two systems hereinbefore described.

Upon completion of the heating operation the hot water obtained may be utilized for its intended purpose at the pressure it is obtained or its pressure may be increased or may be reduced commensurate with its temperature to any extent desired.

When saline waters which form a soft deposit in the tubes are being heated in the indirect heat exchanger, the water is shut off from the tube after a period of operation of a day, several days or a week or more, and the soft layer is flushed out. This flushing may be accomplished by cutting out the sea water supply, opening a valve to waste at one end of the heat exchanger and admitting steam at the other end until the exhaust is free of suspended matter. It has been found that three successive blows of one minute, thirty seconds, and thirty seconds, with the steam pressure allowed to build up to a convenient head of pressure of about 65 p. s. i. prior to each break, is effective in removing the said deposits. The flushing may alternatively be accomplished by the use of other fluids such as high velocity air or water. The flushing can also be accomplished simply by quickly opening an end valve to release the pressure suddenly. The water flashes forming a high velocity steam-water mixture which, on leaving the tube, flushes out the soft deposit. Regardless of the method used, the flushing can be accomplished in a very short time and tube replaced in service. For greater efficiency of operation the heat exchanger should contain a bank of tubes, as of ten or more. With this provision, the flushing of the individual tubes can be accomplished without interrupting or altering the continuous, constant flow of the hot water, provided the exchangers are so designed and arranged that any single series of tubes can be easily cut out of the heating circuit and flushed to remove the soft deposits without interfering with the operation of the other tubes.

The soft deposits formed are composed principally of magnesium hydroxide and contain calcium carbonate combined with silica, iron, aluminum oxides and similar material from the raw salt water. Slight amounts of these compounds may deposit as a hard adherent scale, the amount formed depending upon the salinity of the water and the specific control employed as to the temperature to which the water is heated. The composition of the soft sludge and hard scale is similar for the same water, but at lower salinities magnesium hydroxide is the main constituent whereas at higher salinities calcium carbonate is the principal constituent of the deposits.

Since the flushing operation does not remove hard scale there is a slow gradual build up of this scale which leads to a general decline in the heat transfer rate. The infrequent necessity for removing the hard scale is not prohibitive to commercial operations regardless of the degree of salinity of the salt water being heated. Since the scale

is substantially free of hard, tenacious, chemically-resistant calcium sulfate, its removal may be easily accomplished.

In accordance with a special procedure the ultimate temperature to which the salt water may be heated without prohibitive hard scale formation is increased by the addition of sodium chloride to the said water prior to the heating operation. The amount of additional salt needed will depend on both the salinity of the sea water and upon the maximum temperature to which the water is to be heated. Although the salt to be added may be obtained from any suitable source, the instant invention contemplates obtaining such salt from wells drilled into the relatively pure sodium chloride formations always found beneath the sulfur bearing caprock of salt dome structures and saturating a small part of the brackish water requirements by pumping the same into and out of the salt well in the standard manner for obtaining saturated brines. This minor percentage of sea water thus saturated with sodium chloride is then mixed with the major current of sea water prior to heating.

In carrying out the process of the present invention it may be advantageous in the treatment of some saline waters to employ a stabilizing agent for obtaining better control of scale deposition in the heat exchanger. Any of the several compounds known to inhibit or minimize scale deposition in water heating systems may be employed, for example, any of the group known as glassy phosphates.

The principal embodiments of the present invention may be carried out in accordance with the accompanying flow sheet drawing wherein the heaters, other equipment and lines are shown diagrammatically.

In accordance with a preferred embodiment, the sea or marsh water or other saline water to be heated and employed in the mining of sulfur, after being collected by a suitable system of pumps and screens and settled in a reservoir for the removal of heavy silt is pumped through the inlet pipe **10** into and through a screen box **11** into the top of a direct contact preliminary heater as shown. This heater is provided with superimposed spaced layers of contact material **12**, **13** and **14**. The water sprayed into the tower is first heated by waste flue gases introduced into the tower through the pipe **15** and is then raised to a higher temperature by oxygen-free combustion gases produced in the tower from fuel and air introduced at inlet **16**. The heated water descends to the bottom of the tower where a settling pool is formed and the algae and other colloidal matter settle out below the cone **17**.

The thus heated water leaving the tower at a point above the bottom flows through the conduit **18** to the pressure raising pump **19** and thence to the indirect heat exchanger **21**. In transit, an addition of an acidifying agent is effected either from the inlet pipe **22** or **23** or from both. When the acidifying agent is a gas it is preferably introduced through the pipe **23** after the pressure has been applied to the water.

After being partially heated in the heat exchanger **21** the saline water flows through the conduit **24** to the indirect heat exchanger **26** wherein the water is heated to the temperature required for sulfur mining. Heat exchanger **21** is preferably supplied with low pressure steam and exchanger **26** with high pressure steam.

The heated water leaving the heat exchanger **26** flows through surface line **27** to the sulfur well. The surface line may be coated with Lumnite or other resistant cement but if such coating is not used, protective scale is formed in such pipe by the introduction of an alkali or other precipitating agent through the pipe **28** connected to the pipe **29** at a point adjacent the heat exchanger **26**.

The hot water in the surface line **27** is forced into the hot water casing **31** which conducts the same into the sulfur bearing formation of the mine where it is discharged and melts the sulfur. The sulfur collects in a pool at the bottom of the well and is forced by the water pressure some distance upwardly in the interior concentric pipe **32**. With the addition of air forced into the pipe **32** discharging from a pipe **33**, the molten sulfur is brought to the surface and discharged through the pipe **34**.

The interior of the water conveying pipe **31** and the exterior of the sulfur conveying pipe as well as other auxiliary equipment (not shown) with which the hot saline water comes in contact is coated with a protective scale formed from the hot water by the addition of alkali at one or more points in the pipe **27** as through the pipes **36** and **37**.

The waste flue gases and steam used in the process are produced in the boiler **38**. The waste flue gases flow from the boiler in the pipe **15** leading to the direct heater already described. The steam leaves the boiler in the conduit **39** and part of the same is used to actuate a turbine or other prime mover **41** which in turn actuates an air compressor **42** supplying air through the pipe **43** to the air line **33** of the sulfur well.

The remainder or other part of the steam in the conduit **39** flows through by-pass **44** into the conduit **46** leading to the heat exchangers **26** and **21**. The steam leaving the heat exchanger **26** passes through the conduit **47** to the exchanger **21**. A by-pass **50** supplies additional steam to indirect heat exchanger **21**. The spent steam from this exchanger flows through the conduit **48** into the condensate tank **49** from which the condensate is returned through the pipe **51** to the boiler **38**. The water required for initial boiler feed and for make-up is introduced into the line **51** through the inlet pipe **52**.

The boiler feed make-up, however, may be derived through the utilization of the condenser **53** connected to the direct contact primary heating tower. Within the tower at a point between the packed sections **13** and **14**, part of the combustion gases, substantially saturated with steam, are withdrawn through the pipe **54**, flow through the condenser **53** and give up substantial amounts of condensate suitable after conventional treatment for boiler use. This condensate flows from the condenser **53** through the pipe **56** to the condensate tank **49**. The production of boiler feed water in the condenser **53** involves no heat loss to the process, for the gases are returned from the condenser to the tower through conduit **57**, and the cooling medium employed in the condenser utilizes a portion of the saline water feed flowing from the pipe **10** through the branch conduit **58** which after leaving the condenser **53** flows through pipe **59** discharging into the tower at a point or points in the tower where temperatures are suitable.

A portion of the saline water feed is advantageously conducted through the conduit **61** into the heating tower at a level opposite that at which the supplemental combustion gases are produced. The spraying of the water at this point assists in preventing deterioration of the equipment due to the very high heat of the combustion gases.

The coagulated colloidal matter settled out in the heating tower is periodically removed through the sludge blowdown discharge pipe **62**.

In a simple embodiment of the invention applicable to some saline waters and utilizable where sufficient natural fresh water is available for the boiler feed make-up, the preliminary direct heating system may be by-passed and the saline water, after the settling and screening operations, is introduced directly through the line **63** into the pipe **18** leading to the pressure raising pump **19** connected to the indirect heat exchanger **21**.

With reference to the process in relation to the apparatus and equipment illustrated in the drawing, it should be understood that conventional auxiliary equipment is contemplated although not illustrated, such equipment being the usual deaerators, boiler feed water treatments,

blowdown arrangements, controls, pumps, pressure regulators, steam traps, valves and the like. Part of the steam or the waste steam, furthermore, may be utilized in ways not illustrated on the drawing such as for the heating of any of the sulfur lines or treating vessels which may be steam jacketed or for the operation of any or all of the pumps illustrated.

Example 1

A natural water of 1900 G. P. G. salinity was mixed with 0.16 pound of hydrochloric acid per thousand gallons of water and then pumped under superatmospheric pressure into and through an indirect heat exchanger system composed of four tubular heaters in series of a total length of 640 feet, the rate of flow being 45 gallons per minute and its velocity being 7.1 ft./sec. Heat was applied to the tubes by transfer from steam and the water (at an initial temperature of 85° F.) was heated to 225° F. in the first heater, to 262° F. in the second heater, to 289° F. in the third heater and to 315° F. in the last heater. The run was continued for a period of 17 days. The deposition of soft sludge occurred at a very slow rate and it was not necessary to flush the exchanger oftener than every seven days. Examination of the tubes showed that the amount of permanent scale formed therein was so slight that none could be removed by conventional practice.

When a substantially identical run was carried out but using no acidic addition, to demonstrate the effectiveness of the present invention, it was determined that the deposition of scale occurred so rapidly that daily flushing would not maintain adequate heat transfer rates, and hard scale formed in the four tubes ranged from .02 inch to .08 inch in thickness.

For successful utilization of the hot water of this example for the mining of sulfur, the water is treated as it leaves the exchanger with sodium carbonate at the rate of about 0.35 pound of soda ash per thousand gallons of water. The conduct of this water through the lines leading to the sulfur well forms a thin adherent protective scale on all exposed surfaces. The hot water obtained at the well is then forced into the sulfur bearing formation in the usual way and the molten sulfur rises to the surface with the aid of the air.

Example 2

A natural water of 1100–1400 G. P. G. salinity was introduced into a direct fired flue gas heater in a quantity of 7.5 G. P. M. at a velocity of 7.2 ft./sec. The water was heated therein from an initial temperature of 60° F. to 188° F. The preliminarily heated water was then forced under superatmospheric pressure into and through the indirect heat exchanger defined in Example 1. The four outlet temperatures from the four heaters were respectively 262° F., 290° F., 315° F., and 325° F. Heaters numbers 1 and 2 were under a steam pressure of 75 p. s. i. maximum, heater number 3 was under 90 p. s. i. maximum and heater number 4 under 100 p. s. i. maximum.

As the heating continued over a period of six days, the steam pressure was increased, to compensate for scale formation, up to the said maximums at which time the heaters were flushed with steam. No deposition of hard scale was observable in the first three heaters. In the fourth heater only a slight amount formed. The amount of such scale in this one heater expressed as the percentage loss in heat transfer rate during the run and not recovered by flushing was only 10%.

In a comparative run in which the preliminary heating in the indirect fired flue gas heater was omitted, otherwise involving the same controls and temperatures, the tubes required flushing every sixteen hours to maintain acceptable heat transfer rates. The amount of hard scale formed in each of the tubes was substantial. Expressed as the percentage loss in heat transfer rate during the run (which lasted seven days) and not recovered by flushing, the amount of scale formed in the four heaters respectively was 25%, 56%, 50% and 40%.

The heated water obtained in accordance with this example may be conveyed to a sulfur well through scale protected pipes and utilized in the mining of sulfur as described in Example 1.

Example 3

Sea water was introduced into a direct fired flue gas heater at an initial rate of 9.5 G. P. M. and was heated therein to 185° to 190° F. by the flue gases containing carbon dioxide. The preliminarily heated water was then forced under superatmospheric pressure into and through an indirect heat exchanger composed of two tubular heaters in series, the first of which was heated by steam at a constant pressure of 50 p. s. i. and the second of which was heated at a constant pressure of 90 p. s. i.

As the run continued and scale formed, the rate of the water speed was reduced as required to maintain the effluent water at 325° F. When the rate fell to 5 G. P. M. the flow of water was stopped and the tubes were flushed either with steam or with water. The results obtained after seven days operation indicated that although more frequent flushes were necessary and somewhat more hard scale formed, the operation could be considered commercially successful.

The heated water obtained in accordance with this example may be conveyed to a sulfur well through scale protected pipes and utilized in the mining of sulfur as described in Example 1.

Example 4

The process of the foregoing example was modified except that the water at the temperature of 190° F. leaving the flue gas heater was mixed (after superatmospheric pressure has been applied thereto) with additional carbon dioxide in the proportion of 12 to 18 P. P. M. from a cylinder of compressed carbon dioxide. After a period of two weeks operation it was determined that only one flushing was needed to maintain desirable heat transfer rates.

This example revealed that under some methods of operation, the supplemental addition of carbon dioxide to the water preheated with flue gas is desirable for obtaining superior operational results.

The heated water obtained in accordance with this example may be conveyed to a sulfur well through scale protected pipes and utilized in the mining of sulfur as described in Example 1.

Example 5

Mississippi river water containing 130 P. P. M. hardness as calcium carbonate and 31 P. P. M. of chlorides as NaCl was first heated in a slat packed tower to 140° F. by contacting the same with a countercurrently flowing stream of waste boiler plant flue gases. The thus heated water was then further heated to 190° F. by contacting the same in a similar manner with combustion gases from a natural gas burner adjusted such that the air was limited to the theoretical amount providing combustion gases free of both oxygen and carbon monoxide.

The acidified, preliminarily heated water obtained in this manner was next forced under superatmospheric pressure into a series of three indirect heat exchangers and heated therein to an ultimate temperature of 325° F. The rate of water flow was 9.5 G. P. M. and the steam pressures on the three successive heat exchangers were 50, 90, and 100 p. s. i. respectively. At the end of one week of operation, there was no appreciable deposition of scale in the exchanger and there was no evidence of corrosion.

Combustion gases produced in the direct fired heater hereinbefore defined, removed at a temperature of about 190–195° F., contained a substantial proportion of water vapor (67% by volume) taken up from the saline water treated. By cooling these waste gases, the water therein was condensed. The process serves as a source of fresh

water for the boilers providing the steam for the indirect heat exchangers. This condensation may be effected in another indirect heat exchanger cooled by means of saline water and the partially heated saline water thereby obtained may be further treated and heated in accordance with the present invention, or it may be utilized for any other desirable purposes.

When the sea water is preheated to 190° to 195° F. by a combination of waste flue gases and additional oxygen-free combustion gases, such as defined in Example 5, a number of advantages are obtained. The over-all plant thermal efficiency is increased to an amount greater than 90% and the heat losses out of the stack are less than about 5%. The amount of water output of the plant for the same number of boilers is increased.

The stripping action of the inert burner gas in heating the water to a point near its flash point reduces the oxygen content of the saline water from about 8 P. P. M. in the raw water to less then 0.1 P. P. M. in the heated water ultimately obtained. As a result the corrosiveness of the hot saline water is very substantially reduced.

The lowering of the pH value to 6.6–6.8 by the addition of acid or carbon dioxide reduces the amount of scale produced to an extent that extremely long runs in the exchanger may be made without interruptions for cleaning. With some water under preferred operations in exchangers of best design, the cleaning need not be effected oftener than at 1 to 3 month intervals.

The preliminary heating of the saline water in the direct heating tower, by flocculating the algae and colloidal silt and making their removal from the system a simple matter, provides an improvement in the operation of the indirect heat exchangers by reducing the amount or rate of scale formation.

It should be understood that the present invention in its broader embodiments is not limited to any specific order of application of pressure and the addition of acid, nor to the specific details herein given, but that it extends to all equivalent conditions and procedures which will occur to those skilled in the art upon consideration of the terms herein and the scope of the claims appended hereto.

The claims:

1. A process for reducing the rate of hard scale deposition on surfaces of the tubes of indirect heat exchangers in the heating of alkaline saline waters to temperatures of at least 250° F. which comprises, increasing the hydrogen ion concentration of the water to a pH value of about 6.5–7.5, forcing the water under superatmospheric pressure into a tube of the heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added acid substance but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation.

2. A process for reducing the rate of hard scale deposition on surfaces of the tubes of indirect heat exchangers in the heating of alkaline saline waters to temperatures of at least 250° F. which comprises, adding a small amount of a mineral acid to the water thereby reducing its pH value to about 6.5–7.5, forcing the water under superatmospheric pressure into a tube of the heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added acid but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation.

3. A process for reducing the rate of hard scale deposition on surfaces of the tubes of indirect heat exchangers in the heating of alkaline saline waters to temperatures of at least 250° F. which comprises, introducing carbon dioxide into the water thereby reducing its pH value to about 6.5–7.5, forcing the water under superatmospheric pressure into a tube of the heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added carbon dioxide but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation.

4. A process for heating alkaline saline waters in indirect heat exchangers to temperatures of at least 250° F. without causing substantial hard scale deposition on the surfaces of the tubes thereof which comprises adding an acidic substance selected from the group consisting of mineral acids and substances forming such acids in aqueous solution to the water in a quantity which reduces the pH of the water to a value of about 6.5–7.5, forcing the water under superatmospheric pressure into a tube of the heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added acid substance but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation.

5. A process for heating alkaline saline waters in indirect heat exchangers to temperatures of at least 250° F. without causing substantial hard scale deposition on the surfaces of the tubes thereof which comprises, adding a small amount of a mineral acid to the water in a quantity which reduces the pH of the water to a value of about 6.5–7.5, forcing the water under superatmospheric pressure into a tube of the heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added acid but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation.

6. A process for heating alkaline saline waters in indirect heat exchangers to temperatures of at least 250° F. without causing substantial hard scale deposition on the surfaces of the tubes thereof which comprises, introducing carbon dioxide into the water in a quantity which reduces the pH of the water to a value of about 6.5–7.5, forcing the water under superatmospheric pressure into a tube of the heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added carbon dioxide but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation.

7. A process for heating alkaline saline waters in indirect heat exchangers to temperatures of at least 250° F. without causing substantial hard scale deposition on the surfaces of the tubes thereof which comprises, preliminarily heating said water by directly contacting the same with combustion gases containing carbon dioxide gas whereby carbon dioxide is dissolved in said water and its

pH value reduced to about 6.5–7.5, forcing the thus treated water under superatmospheric pressure into a tube of an indirect heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added carbon dioxide but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation.

8. The process defined in claim 7 wherein the preliminary heating with combustion gases is to a temperature of 170° to 195° F.

9. A process for heating alkaline saline waters in indirect heat exchangers to temperatures of at least 250° F. without causing substantial hard scale deposition on the surfaces of the tubes thereof which comprises, preliminarily heating said water by directly contacting the same with combustion gases containing carbon dioxide gas substantially free of oxygen gas, whereby carbon dioxide is dissolved in said water and its pH value reduced to about 6.5–7.5, forcing the thus treated water under superatmospheric pressure into a tube of an indirect heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added carbon dioxide but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation.

10. The process defined in claim 9 wherein the preliminary heating with combustion gases is to a temperature of 170° to 195° F.

11. A process for heating alkaline saline waters in indirect heat exchangers to temperatures of at least 250° F. without causing substantial hard scale deposition on the surfaces of the tubes thereof which comprises, preliminarily heating said water by directly contacting the same with waste flue gases, further heating the said water to a higher temperature by directly contacting the same with carbon dioxide burner gases substantially free of oxygen gas, whereby carbon dioxide is taken up and dissolved in said water and its pH value reduced to about 6.5–7.5, forcing the thus treated water under superatmospheric pressure into a tube of an indirect heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added carbon dioxide but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation.

12. A process for heating alkaline saline waters in indirect heat exchangers to temperatures of at least 250° F. without causing substantial hard scale deposition on the surfaces of the tubes thereof which comprises adding an acidic substance selected from the group consisting of mineral acids and substances forming such acids in aqueous solution to the water in a quantity which reduces the pH of the water to a value of about 6.5–7.5, forcing the water under superatmospheric pressure into a tube of the heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added acid substance but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation, and periodically flushing out any soft layer of scale-forming compounds deposited in said tube.

13. A process for heating alkaline saline waters in indirect heat exchangers to temperatures of at least 250° F. without causing substantial hard scale deposition on the surfaces of the tubes thereof which comprises, preliminarily heating said water by directly contacting the same with combustion gases containing carbon dioxide gas whereby carbon dioxide is dissolved in said water, adding a mineral acid to said heated water in a quantity which reduces the pH to a value of about 6.5–7.5, forcing the thus treated water under superatmospheric pressure into a tube of an indirect heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added acid substance and carbon dioxide but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation.

14. A process for heating alkaline saline waters in indirect heat exchangers to temperatures of at least 250° F. without causing substantial hard scale deposition on the surfaces of the tubes thereof which comprises, preliminarily heating said water by directly contacting the same with combustion gases containing carbon dioxide gas whereby carbon dioxide is dissolved in said water, applying superatmospheric pressure to said treated water, adding an acidic substance selected from the group consisting of mineral acids and substances forming such acids in aqueous solution to the pressurized water thereby reducing its pH value to about 6.5–7.5, conducting the thus treated water under superatmospheric pressure into a tube of an indirect heat exchanger and while the water is in said tube, heating the same to a temperature above 250° F. at which scale deposition would occur in the absence of the added acid substance and carbon dioxide but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, and maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation.

15. In the mining of sulfur by means of superheated water pumped down into the sulfur-bearing formation, the continuous process which comprises, increasing the hydrogen ion concentration of an alkaline saline water to a pH value of about 6.5–7.5, forcing the water under superatmospheric pressure into a tube of a heat exchanger and while the water is in said tube, heating the same to a sulfur-melting temperature required in sulfur mining at which scale deposition would occur in the absence of the added acid substance but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation, and pumping the resulting heated water while still under pressure into the sulfur-bearing formation.

16. The process defined in claim 15 wherein the hydrogen ion concentration of the water is increased by the addition of a small amount of a mineral acid.

17. The process defined in claim 15 wherein the hydrogen ion concentration is increased by the introduction of carbon dioxide into the water.

18. In the mining of sulfur by means of superheated water pumped down into the sulfur-bearing formation, the continuous process which comprises, increasing the hydrogen ion concentration of an alkaline saline water to a pH value of about 6.5–7.5, forcing the water under superatmospheric pressure into a tube of a heat exchanger and while the water is in said tube, heating the same to

a sulfur-melting temperature required in sulfur mining at which scale deposition would occur in the absence of the added acid substance but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation, adding to the heated water an alkali in a quantity and for a period which causes deposition of a thin protective scale on exposed surfaces of conveying pipes and forcing the resulting water through the resulting protected pipes while still under pressure into the sulfur-bearing formation.

19. In the mining of sulfur by means of superheated water pumped down into the sulfur-bearing formation, the continuous process which comprises preliminarily heating an alkaline saline water by flowing the same downwardly in direct contact with combustion gases, passing the heated water through a settling pool, decanting the heated water from said pool while leaving organic sludge in said pool, increasing the hydrogen ion concentration of the alkaline saline water to a pH value of about 6.5–7.5, forcing the water under superatmospheric pressure into a tube of a heat exchanger and while the water is in said tube, heating the same to a sulfur-melting temperature required in sulfur mining at which scale deposition would occur in the absence of the added acid substance but below a temperature which causes appreciable calcium sulfate scale deposition during the heating operation, maintaining the temperature of the heating surfaces in contact with the saline water below that which causes the calcium sulfate present to precipitate out during the heating operation and pumping the resulting heated water while still under pressure into the sulfur-bearing formation.

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