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HEATING OF SEA WATER FOR SULFUR MINING

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This invention relates to improved processes for heating sea and other waters of high salinity in indirect or tubular heat exchangers to provide hot process water for use in sulfur mining. Such waters cannot be heated successfully in tubes by conventional heating procedures, for hard scale forms at a prohibitive rate when the temperature is raised to the high levels employed in such mining operations.

In my prior joint application with Vas Hubert Brogden, Serial No. 253,306, filed October 26, 1951 (Patent No. 2,756,035), we described a process directed at the problem of acomplishing this same result, involving first, adding an acidifying agent to the saline water which reduces the hydrogen ion concentration of the water to a pH value between about 6.5 and 7.5 and then heating the treated water under superamospheric pressure during passage through the tubes of a series of heat exchangers to a final temperature above about 250° F. while maintaining the temperature of the heating surfaces of the tubes in contact with the saline water below that which causes the calcium sulfate present in the saline water to precipitate out during the heating operation or attach as a hard scale on the heating surfaces.

In my prior application Serial No. 245,090, filed September 4, 1951 (Patent No. 2,756,207), of which the present application is a continuation-in-part, I described a process, also directed to the problem described above, involving the heating of saline waters by passing such water under superatmospheric pressure through a series of tubes in an indirect heat exchanger in which the saline water inside of the tubes is maintained at a temperature below that at which excessive hard scale deposition occurs and in which the saline water is heated under superatmospheric pressure to an ultimate temperature above 250° F. at which calcium sulfate would normally form a hard scale but below that at which calcium sulfate present in the altered saline water forms such scale, the result being that those salts which deposit in the tubes are composed substantially only of soft, non-adherent materials which can be flushed out periodically merely by forcing fluids rapidly through the tubes in which the deposition has occurred. In this application it is disclosed that the avoidance of deposition of scale can be facilitated further by the addition of sodium chloride or of concentrated salt dome to the saline water.

Whereas these prior processes have proven completely successful for the heating of saline waters available in certain areas, and for the mining of sulfur under limited conditions, it has since become apparent that an improved process is needed which has greater flexibility in connection with the mining of sulfur and is capable of operating under other conditions, including the use of saline or sea waters of higher salinity.

Improvement through the addition of sodium chloride has limitations of economic character and as to the addition of raw salt dome brine, there is a limit upon the benefit obtainable, since the amount that can be added to the sea water is limited due to the resulting excessive increase in specific gravity imparted to the process water, in relation to successful use in sulfur mining.

The objects of the present invention include the provision of processes capable of providing saline waters at higher sulfur mining temperatures and capable of utilizing waters of higher salinity, constituting improvements in the processes of the hereinbefore mentioned applications wherein saline water is heated to sulfur mining temperatures in tubes of indirect heat exchangers without causing excessive rates of calcium sulfate deposition.

In the preferred and most practical embodiment of the present invention, the sea or other high salinity water to be heated in a continuously flowing stream is supplemented by the addition of a small proportion, e.g. 0.1–10% of a concentrated salt dome brine the calcium sulfate content of which has been substantially reduced and is low in relation to saturation, or, e.g. below about 2000 mg./l. calcium, calculated as $CaCO_3$. The sea water containing the brine is thereafter treated by the addition of an acidifying agent as sulfuric acid, in a quantity which increases the hydrogen ion concentration to a pH value of about 6.5–7.5 and the treated water is then forced under superatmospheric pressure into and through a series of heating tubes of a heat exchanger in which the heating surfaces of the tubes in contact with the treated saline water are maintained below that which causes appreciable precipitation of the calcium sulfate present in the water.

Because of the addition of the salt dome brine of low calcium sulfate content to the sea water, the temperature to which the sea water can be heated for providing sulfur mining process water and without causing scaling is substantially increased, and depending upon how high the salt content of the sea water treated is, process water at temperatures of from 280°–360° F. can be provided without causing scaling difficulties in the heaters.

The concentrated brine may be obtained from the salt dome by conventional procedures, using any available source of water which normally would be of the same origin as the sea or other saline water used for the mining process. Saturated brine is preferably employed for reasons of efficiency, but brines of only twenty percent NaCl or less can be used to advantage. For the mining of sulfur by conventional procedures, the amount of the brine added to the sea or other saline water and its sodium chloride content should be such as will not produce process water of too great a specific gravity, that is one having more than about 5% NaCl.

More in detail, the concentrated salt dome brine of excessive calcium sulfate content in relation to saturation is treated to take out the excessive calcium content by reacting the calcium sulfate to be removed with sodium carbonate or soda ash, and settling or filtering to remove the calcium carbonate precipitate formed. This treatment, suitably, can remove as much as 85% of the calcium, but it may be advisable for reasons of economy, in relation to equipment available or other factors, to remove a lesser amount, or as low as 20% of the calcium.

In a limited alternative or supplementary concept, the present invention contemplates lessening the quantity of calcium sulfate in relation to that of the sodium chloride present in the salt or other saline water being converted into hot process water for sulfur mining, by reducing the actual quantity of calcium sulfate in the said sea water. This reduction in calcium sulfate content may be effected by treatment of the sea water with sodium carbonate, or less satisfactorily, with magnesium carbonate or with a sodium ion exchange material either of the resin type of the zeolite type, each of which procedures converts the dissolved calcium sulfate into a soluble sulfate and an insoluble calcium compound which is removed from the treated water, as by settling or filtering action. Under this method of procedure it is ordinarily sufficient