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METHOD OF INHIBITING DISSOLUTION OF CALCIUM SULFATE

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This invention relates to a method for inhibiting the dissolution of calcium sulphate in aqueous solutions, and more particularly relates to a method for inhibiting the dissolution of calcium sulphate into a brine produced by dissolving an alkali-metal halide, especially sodium chloride, with water.

High purity brines are required for many processes and industrial uses. Sodium chloride brine, for instance, is used in the production of metallic sodium, chlorine, numerous sodium compounds, such as soda ash, caustic soda and sodium chloride, and is also used in the production of sulphur by the Frasch process. One method of preparing brine is by the dissolution of underground salt masses with fresh or sea water which is injected into the mass, the brine formed being withdrawn as a concentrated solution.

All natural alkali-metal halides are relatively impure. Among the most troublesome contaminating materials is calcium sulphate which may be present in amounts up to 1% or more, that is, 10,000 parts per million or more. Calcium sulphate is only slightly soluble in fresh water but is more soluble in brine, its solubility increasing as the salt concentration of the brine is increased. Calcium sulphate becomes less soluble in either fresh water or brine as the temperature of the solution is raised. Thus, if a solution nearly saturated with calcium sulphate is heated, calcium sulphate precipitates gradually. Precipitation of the calcium sulphate during crystallization of salt from brine will cause contamination of the salt being crystallized. Moreover, the calcium sulphate tends to precipitate on the walls of heaters and associated equipment as a glass-hard, continuous scale that interferes with heat transfer and reduces the open area of conduits through the equipment.

The low solubility of calcium sulphate precludes economical removal of the scale from equipment surfaces. Not only is the calcium sulphate only slightly soluble in water, it is also impervious to acids and is very slowly attacked by strong bases, even when hot. Mechanical methods are generally resorted to for its removal, but these must be so violent, due to the extreme hardness of the scale, that the equipment being cleaned is frequently seriously damaged.

Solutions proposed to date to cure the problem have consisted in attempts to inhibit the precipitation of the calcium sulphate after it has been dissolved in the solution. These methods have been found to be expensive, time consuming and inefficient. Attempts have been made to solve the problem by preventing the calcium sulphate from dissolving in the brine in the first place. One method utilizes sodium carbonate or phosphate added to the aqueous solvent prior to bringing it into contact with the contaminated halide to be dissolved. Another method utilizes sodium polyphosphates in the same way. Both methods have the disadvantage that if the water being used as the solvent contains appreciable calcium, the additive will be precipitated before it contacts the calcium sulphate particles.

Accordingly, it is an object of this invention to provide a method for inhibiting the dissolution of calcium sulphate into an aqueous solvent during the dissolution of salt (i.e., sodium chloride or other alkali-metal halide) into the aqueous solvent.

It is a special object of this invention to reduce the rate at which calcium sulphate is dissolved in aqueous solutions while dissolving alkali-metal halides.

It is a further object of the present invention to provide a method of preparing a brine from a solid salt, especially sodium chloride in which the dissolution of calcium sulphate into the resulting brine is inhibited.

Other objects will be apparent to those skilled in the art from reading the following description taken in conjunction with the drawings, in which:

FIGURE 1 is a graph showing the effect of additive concentration on the solution of calcium sulphate, and

FIGURE 2 is a graph which shows the influence of time and the use of one of the additives of the invention on the dissolution rate of calcium sulphate.

The present invention results from the discovery that a class of compounds, unrelated to any of those known for the purpose before, reduces the rate of dissolution of calcium sulphate during the process of dissolving the alkali-metal halide with which the calcium sulphate is usually present. The members of this class of compounds vary from one another in cost, commercial availability, stability at elevated temperatures, and degree of calcium sulphate solution rate reduction, thus making it possible to choose from among the class, a compound which is most economical and suitable for a particular purpose.

It has been found that the dissolution of calcium sulphate present as an impurity in natural alkali-metal halide formations can be inhibited by introducing into the solvent small quantities of alkali-metal or ammonium salts or hydrogen ion compounds which are made up of certain active groups attached to at least one hydrocarbon group containing between 2 and 30 carbon atoms per active group. The active groups which are useful in the practice of this invention includes the sulfonates, sulfates, carboxylates, orthophosphates, phosphites, phosphonates, and phosphonites. The hydrocarbon group may be substituted or unsubstituted and may be aliphatic, alicyclic, aromatic or heterocyclic.

It has been further found that for the inhibiting compound to be useful in the practice of this invention, the product of its reaction with the calcium present must be less soluble than calcium sulphate under the conditions of use.

The inhibiting compound used must be soluble to the extent of at least 2 milligrams per liter of solution. The inhibiting compound may be present at a concentration of 2 to 1000 milligrams or more per liter of solution, and preferably is present in a concentration range of 5 to 100 milligrams per liter. Amounts in excess of 1000 milligrams per liter usually do not provide any useful purpose and are wasteful. The solution in which the inhibiting compound is used should contain not less than three weight percent of the alkali-metal halide by the time that it is withdrawn from contact with the undissolved calcium sulphate.

The inhibiting compound may be dissolved in the aqueous solvent before the aqueous solvent is brought into contact with the halide to be dissolved, or the calcium sulphate-contaminated alkali-metal halide may be mixed with the compound in either its solid form or in concentration solution prior to bringing the water into contact with the alkali-metal halide.

Inhibiting compounds found operable in the practice of this invention include:

(1) Carboxylates:
- (*a*) Sodium polyacrylate
- (*b*) Sodium carboxymethyl cellulose
- (*c*) Sodium caseinate
- (*d*) Sodium salt of picolinic acid
- (*e*) Sodium salt of 2-thiophene-carboxylic acid
- (*f*) Sodium salt of aminooctanoic acid