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A NEW AND NOVEL PROCESS FOR SEPARATION OF SALTS, SCALE SALTS AND NORM CONTAMINANT SALTS FROM SALINE WATERS AND SALINE SOLUTIONS

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ABSTRACT

A new and novel process for saline waters and saline solutions conversion has been provided that requires only a fair amount of a miscible organic solvent and heat transfer. Such requirements are ordinary in the nature of precipitation and vaporization. The proposed process consists of adding a miscible (strongly associated) organic solvent to saline water so that salt precipitates of the saline water are formed. The resultant salt precipitates (pure solids) are then separated from the organic-water mixture. After separating the salt precipitates, the miscible organic solvent is removed and recovered from the organic-water mixture. The recovered miscible organic solvent can then be returned to the process, and water is stripped out of trace of miscible organic solvent, and removed from the system as product water.

The proposed process is potentially suited for the precipitation and separation of salts, scale salts, and NORM contaminant salts form saline water and saline solution as well as for the remediation of contaminated soils.

INTRODUCTION

Water is the inheritable solvent for a wide variety of dissolved salts, simple and complex. Saline waters such as sea water, brine water, oil-field brine water, formation water, brackish water, ground water, salt lake water, make-up saline solution, and the like are usually high in some of the following species: (1) Salts: chlorine salts, sulfate salts, carbonate salts; (2) Scale Salts: barium, calcium, and strontium in the form of sulfates, carbonate and silicates; and (3) Naturally Occurring Radioactive Materials (NORM) contaminant salts, or the decay chain of uranium (^{238}U, ^{234}Th, ^{234}U, ^{230}Th, ^{226}Ra, ^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po, ^{210}Pb, ^{210}Bi, ^{210}Po, and ^{206}Pb). Such species are rendering saline waters either unusable (e.g., high total dissolved solids) or posing serious disposal problems (e.g., disposing brine stream from membrane processes and NORM contaminant salts), industrial problems (e.g., scale formation), and health and environmental concerns.

The scarcity of natural resources of usable water in arid and semi-arid areas has a significant impact on the economic development. Conventional desalination and membrane separation technologies present relatively expensive technologies to separate salts from saline waters, which are applicable primarily on a regional basis. Further, the relatively high cost of water redistribution appears to preclude the economical transportation of water over long distances. Consequently, the agricultural growth in arid areas for instance, is restricted because of a limited usable water supply.

The concentrations of salts and scale salts in saline water are quite high, and thus the permeate (product) stream is limited to about 70% of the overall feed stream in conventional desalination processes such as membrane processes. The disposal of the remaining 30%, which is the brine stream, is a challenging engineering task. The engineering task would include economic considerations, technical difficulties, and environmental regulations. Therefore, a need exists for a process to service as an integral part of hybrid system in conjunction with membrane or other saline water conversion processes to concentrate and reduce further the brine stream. Such a process could significantly mitigate and reduce the disposal problem.

A large volume of saline water is produced and associated with the exploration and production of petroleum, gas, coal, and fossil fuel. Several problems are associated with the produced saline water. First, scale salts and formation have a substantial impact on facilities of petroleum, gas, coal, fossil fuel and other industries since it: (1) restricts production flow; (2) causes equipment inefficiencies; (3) impedes heat transfer; and (4) damages equipment and increases shutdown time. Further, the availability of uranium and thorium in the crust of the earth suggests that NORM contaminant salts will be common wherever produced saline water is salty, hot and depleted in sulfate. The uranium daughters including ^{238}U, ^{234}Th, ^{234}U, ^{230}Th, and ^{226}Ra are chemically active and attached themselves to nearby solid materials. As such, scale salts can become radioactive due to attachments of NORM contaminant salts. Second, the produced saline water can adversely contaminate and affect soil and vegetation. Third, serious health and environmental problems are encountered with produced saline water.

Currently, there is no satisfactory method or process to separate and concentrate scale salts and NORM contaminant salts from saline waters or contaminated soils. Downhole injection is the available option for the disposal of such species. However, economic, technical, and logistic considerations are associated with such an option. Further, downhole injection is an inappropriate for high volume salt streams such as contaminated soils. As such, a process for the separation and concentration of scale salts and NORM contaminant salts from saline waters and contaminated soils is urgently needed. Such a process could concentrate and reduce the scale salts and NORM contaminant salts, and thus could make the downhole injection a more feasible option.

The above situations have led to invent and propose the process that is described in this work to alleviate the problems associated with the use and production of saline waters and contaminated soils [Bader, Patent in Pending; 1994].

PROCESS DESCRIPTION

The proposed process consists of adding a miscible organic solvent to saline water so that salt precipitates of the saline water are formed. The resultant salt precipitates are then separated from the organic-water mixture. After that, the miscible organic solvent is removed and recovered from the organic-water mixture by applying vacuum with or without heating, or by using distillation methods. The recovered miscible organic solvent can then be condensed and returned to the process and water is stripped out of trace of miscible organic solvent and removed from the system as product water. The miscible organic solvent that exists in the product water is essentially at infinite dilution. Applying vacuum or using distillation methods to strip out the miscible organic solvent, however, depend upon the economic feasibility, the required purity of the product water, and the environmental regulations.

There are a number of miscible organic solvents which are appropriate for the use in this invention [Bader; 1994]. The preferred miscible organic solvents are those which: (1) can cause high salt precipitation; and (2) can be vaporized at temperatures near the ambient temperature (e.g., low boiling point, relatively high vapor pressure and relative volatility). The fast vaporization of the miscible organic solvent requires only the application of vacuum, which is considerably more economical than the relatively high cost of heat transfer in the conventional distillation methods. The above factors primarily determine the best candidate among the miscible organic solvents. However, miscible organic solvents with minimal environmental risks (e.g., not carcinogens) and low cost are preferred [Bader, Patent in Pending; 1994].

The precipitation action is carried out as a solid-liquid phase equilibrium process [Bader; 1994]. Several miscible organic solvents in their liquid-phase can be used in this invention. These miscible organic solvents are isopropylamine, propylamine, acetone, methanol, ethanol, acetonitrile, diisopropylamine, tetrahydrofuran, and dioxane. The above miscible organic solvents are listed as examples, and many others are known to be miscible in water and potentially can be employed [Bader, Patent in Pending; 1994].

There are several advantages of using miscible organic solvents in their liquid-phase [Bader, Patent in Pending; 1994]. Such miscible organic solvents: (1) can be employed at different and actual conditions; (2) provide good contact and mixing between species; (3) allow better control over their dose, transportation and handling; and (4) permit better separation of the species in different phases. Preferring miscible organic solvents in the liquid-phase, however, does not preclude the use of other miscible organic solvents in the gas-phase such as dimethylamine, ethylamine, diethylamine, and acetaldehyde, and the like [Bader, Patent in Pending; 1994].

Isopropylamine is the preferable miscible organic solvent among other solvents for the proposed process because of its: (1) high precipitating capability with several salts; (2) low boiling point (32.5°C) and very high relative volatility (84339); and (3) minimal environmental risks. In addition, isopropylamine has been used as a herbicide (isopropylamine salt) for agricultural purposes [Bader, Patent in Pending; 1994].

The precipitation action is unique. With a saline water containing different salts, the addition of a certain amount of isopropylamine will lead to precipitation of these salts in different percentages. For instance, the addition of enough isopropylamine to saline water containing NaCl (fifteen times the original volume of the saline water) will lead to precipitation of more than 94% of NaCl in a pure solid form. It is clear that this single stage process will waste both the miscible organic solvent and the energy required to strip out and recover the miscible organic solvent. Great savings in the amount of the valuable miscible organic solvent and the energy can be achieved by using a multi-stage precipitation process. Thus, it will be more economical for the precipitation of NaCl, for instance, with isopropylamine to precipitate 17.3% in each stage. The ratio of isopropylamine to saline water to precipitate 17.3% of NaCl is 0.2 to 1.

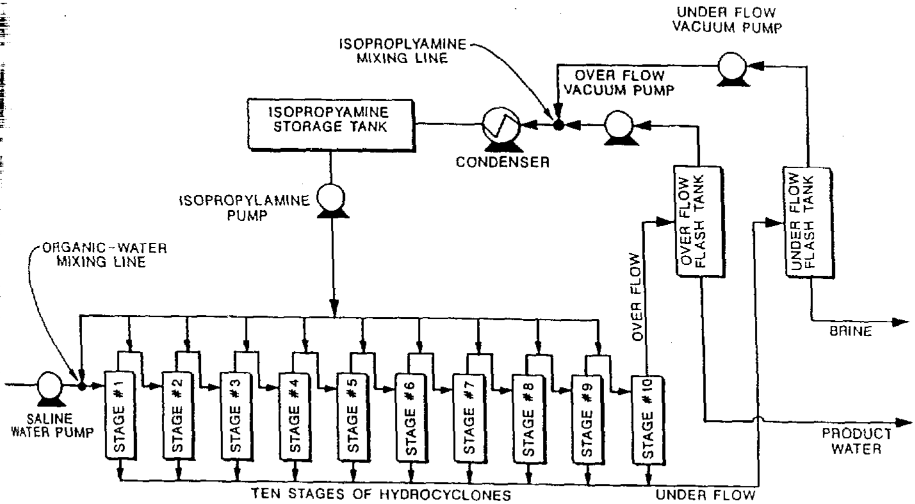

Figure 1. Desalting Saline Water Flow Sheet

This amount of isopropylamine will also lead to precipitate different fractions of other salt species [Bader, Patent in Pending; 1994].

For the purpose of illustration of the proposed process, reference is now made to the flow sheet of the process to desalt saline water as shown in Figure 1 [Bader, Patent in Pending; 1994]. In this process, 27.8 GPM (40,000 GPD) with 5,000 ppm TDS of saline water is pumped using the saline water pump to the first stage of multi-hydrocylcones via the organic-water mixing line where it is contacted with 5.6 GPM of isopropylamine (ratio of 1 to 0.2). The isopropylamine is fed to the organic-water mixing line from the isopropylamine storage tank using the isopropylamine pump.

The precipitated solid salts in the first stage of hydrocyclone are then separated from the over flow organic-water mixture by the multi-hydrocylones. With the multi-hydrocyclone design, the under flow for each stage can be limited to approximately 0.4 GPM. The amount of isopropylamine in the under flow for each stage is about 0.08 GPM and the remainder is water and solid salt precipitates. These calculations are based on a volume basis, taking into account the specific gravity of the liquid (water and isopropylamine) and solid salt precipitates.

Thermodynamic behavior provides us with explicit information regarding the intermolecular interactions that take place in the precipitation process [Bader; 1994]. According to the thermodynamic model that predicts the phase-behavior of precipitation process, the fundamental assumption in the design of the hydrocyclone stages is based on the changes in the chemical potentials (fugacities) in terms of physically measurable quantities such as temperature, pressure and composition [Bader, Patent in Pending; 1994]. At relatively constant temperature and moderate pressure, changing the composition of the miscible organic solvent, combined simultaneously with the change in the composition of the salt due to the precipitation action, will lead to changes in the phase equilibrium of the mixture. Thus, for all of the following stages of the hydrocyclones (stage 2 to stage 10), 0.1 GPM of isopropylamine is added to the overflow in each stage to compensate for the losses in the under flow and to enhance the precipitation process.

Each separation stage contains five hydrocyclones, and each hydrocyclone has a one inch diameter. A valve is installed on the discharge of the under flow chamber to act as a grit pot. With this type of arrangement, one feed pump can be used to the first stage and take the over flow directly into the next stage. Hydrocyclones are able to separate particles ranging from 4 microns to about 600 microns. The advantages of using hydrocyclones in the design of the proposed process are: (1) simplicity; (2) low maintenance (e.g., continuous operation without moving parts); (3) low cost; and (4) easy installation [Bader, Patent in Pending; 1994].

After the last stage of hydrocyclones, the over and the under flows are fed into two different vacuum vessels (liquid-vapor separators). These vessels are the over flow flash tank and the under flow flash tank, which are used, respectively, to strip out and recover the isopropylamine from water and water-solid salt precipitates mixture by using two vacuum pumps.

The recovered isopropylamine (99.91% recovery) is fed into a condenser (a shell and tube heat exchanger) via the isopropylamine mixing line and then returned to the process via the storage tank and the isopropylamine pump.

The product water is removed to the aerated water pond as a product while the brine is removed to a disposable area. The desorption of isopropylamine from the product water in the aerated pond to the air can be aided by a mechanical agitator.

The illustrative example has targeted NaCl, which is the major chlorine salt, the most soluble salt in water, and the least precipitate. The operating costs of the invented process indicate that the major factor is the isopropylamine cost and the amount of heat transfer needed to recover isopropylamine. However, most of saline waters, except may be seawater and/or lake water, are commonly dominated by sulfate salts, carbonate salts, silicate salts and chlorine salts other than NaCl. The solubilities of such salts are much lower than the solubility of NaCl in water, and thus conceptually their solubilities can be drastically reduced (by the precipitation concept) by adding a small amount of a miscible organic solvent. Practically, such species can be easily precipitated from the saline waters using the proposed process with a much lesser number of hydrocyclone stages and a much smaller amount of isopropylamine (or other miscible organic solvents). Therefore, an appreciable reduction in the quantity (and of course the cost) of isopropylamine directly leads to a substantial reduction in the amount of heat transfer, and thus a significant reduction in the capital and operating costs of the proposed process [Bader, Patent in Pending; 1994].

In the case of soil remediation, the soil which is contaminated with salts, scale salts, and NORM contaminant salts can be placed into a lined lagoon and mixed with an excess amount of water to dissolve the salt species and form a make-up saline solution. The lagoon could also serve as clarifier to settle the sediment from the make-up saline solution prior to the precipitation and separation process. After that, the proposed process that is described in this work can be used to precipitate and separate the salt species from the make-up saline solution [Bader, Patent in Pending; 1994].

The proposed process can perfectly lend itself to modular skid-mounted construction. Various changes and modifications may be made in the flow sheet. Saline waters such as sea water, brine water, oil-field brine water, formation water, brackish water, ground water, salt lake water, make-up saline solution, and the like can be used in this invention. Isopropylamine has been mentioned as the miscible organic solvent to be used, however, other miscible organic solvents such as propylamine, acetone, methanol, ethanol, acetonitrile, diisopropylamine, tetrahydrofuran, dioxane and the like may also be employed.

The operating equipment and conditions set forth may be varied to fit different circumstances: (1) the type, concentration, and number of salt species present in the saline waters and saline solutions to be precipitated and separated; (2) the purposes of desalting saline waters and saline solutions such as agricultural, brine concentration, scale removal, industrial, salts recovery, soil remediation, carrier free radioactive material recovery and the like; and (3) different geographical locations and climate conditions.

REFERENCES

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