[0025] It is an object of the present invention to provide a cost-effective and efficient method for the regeneration of alkali metals used in the desulfurization, denitrogenation, and demetallation of hydrocarbon streams. As will be described herein, the present invention is able to remove contaminants and separate out unwanted material products from desulfurization / denitrogenation / demetallation reactions, and then recover those materials for later use.

[0026] Another objective of the present invention is to teach improvements in the process and device for recovering alkali metal from alkali metal sulfide generated by the sulfur removal and upgrading process.

BRIEF SUMMARY OF THE INVENTION

[0027] The present ~~invention~~ disclosure provides a process for removing nitrogen, sulfur, and heavy metals from sulfur-, nitrogen-, and metal-bearing shale oil, bitumen, heavy oil, or refinery streams. The present disclosure ~~invention~~ further provides an electrolytic process of regenerating alkali metals from sulfides, polysulfides, nitrides, and polynitrides of those metals. The present disclosure ~~invention~~ further provides an electrolytic process of removing sulfur from a polysulfide solution.

In one aspect, the present disclosure provides an electrolytic cell for oxidizing alkali metal monosulfide or alkali metal polysulfides comprising: an anolyte compartment configured with an anode and containing an anolyte solution comprising an alkali metal monosulfide, an alkali metal polysulfide, or a mixture thereof and an anolyte solvent that partially dissolves elemental sulfur, the anolyte compartment further comprising an anolyte solution inlet and an anolyte solution outlet; a catholyte compartment configured with a cathode and containing a catholyte, wherein the catholyte comprises a molten alkali metal, the catholyte compartment further comprising a catholyte outlet; an alkali ion conductive membrane configured to selectively transport alkali ions, wherein the alkali ion conductive membrane is substantially impermeable to anions, the anolyte solvent, and dissolved sulfur; a source of electric potential electrically coupled to the anode and the cathode and configured to: oxidize the alkali monosulfide or polysulfide in the anolyte compartment to form liquid elemental sulfur and alkali metal ions; cause alkali metal ions to pass through the alkali ion conductive membrane from the anolyte compartment to the catholyte compartment; and reduce the alkali metal ions in the catholyte compartment to form liquid elemental alkali metal; an elemental sulfur settling zone where liquid elemental sulfur forms a second liquid phase and separates from the anolyte solution; and a sulfur outlet for removal of the liquid

elemental sulfur from the electrolytic cell disposed at a location lower than the anolyte solution outlet.

In another aspect, the present disclosure provides a plurality of coupled electrolytic cells comprising a first electrolytic cell as disclosed herein and a second electrolytic cell as disclosed herein, wherein the anolyte solution inlet of the second electrolytic cell is connected to the anolyte solution outlet of the first electrolytic cell.

In a further aspect, the present disclosure provides a plurality of coupled electrolytic cells comprising a first electrolytic cell as disclosed herein, a second electrolytic cell as disclosed herein, a third electrolytic cell as disclosed herein, and a fourth electrolytic cell as disclosed herein, wherein the anolyte solution inlet of the fourth electrolytic cell is connected to the anolyte solution outlet of the third electrolytic cell, wherein the anolyte solution inlet of the third electrolytic cell is connected to the anolyte solution outlet of the second electrolytic cell, and wherein the anolyte solution inlet of the second electrolytic cell is connected to the anolyte solution outlet of the first electrolytic cell.

[0028] One non-limiting embodiment within the scope of the present disclosure ~~invention~~ includes a process for oxidizing alkali metal sulfides and polysulfides electrochemically. The process utilizes an electrolytic cell having an alkali ion conductive membrane configured to selectively transport alkali ions, the membrane separating an anolyte compartment configured with an anode and a catholyte compartment configured with a cathode. An anolyte solution is introduced into the anolyte compartment. The anolyte solution includes an alkali metal sulfide and/or polysulfide and an anolyte solvent that partially dissolves elemental sulfur and alkali metal sulfide and polysulfide. A catholyte solution is introduced into the catholyte compartment. The catholyte solution includes alkali metal ions and a catholyte solvent. The catholyte solvent may include one of many non-aqueous solvents such as tetraethylene glycol dimethyl ether (tetraglyme), diglyme, dimethyl carbonate, dimethoxy ether, propylene carbonate, ethylene carbonate, diethyl carbonate. The catholyte may also include an alkali metal salt such as an iodide or chloride of the alkali metal. Applying an electric current to the electrolytic cell oxidizes sulfide and/or polysulfide in the anolyte compartment to form higher level polysulfide and causes high level polysulfide to oxidize to elemental sulfur. The electric current further causes alkali metal ions to pass through the alkali ion conductive membrane from the anolyte compartment to the catholyte compartment, and reduces the alkali metal ions in the catholyte compartment to form elemental alkali metal.

[0029] Sulfur may be recovered in the liquid form when the temperature exceeds the melting point of sulfur and the sulfur content of the anolyte exceeds the solubility of the solvent. Most of the anolyte solvents have lower specific gravity compared to sulfur so the liquid sulfur settles to the bottom. This settling may occur within a settling zone in the cell where the sulfur may be drained through an outlet. Alternatively a portion of the anolyte solution may be transferred to a settling zone out of the cell where settling of sulfur may occur more effectively than in a cell.

[0030] The melting temperature of sulfur is near 115 °C so the cell is best operated above that temperature, above 120 °C. At that temperature or above, the alkali metal is also molten if the alkali metal is sodium. Operation near a higher temperature, such as in the 125-150 °C range, allows the sulfur to fully remain in solution as it is formed from the polysulfide at the anode, then when the anolyte flows to a settling zone, within or external to the cell where the temperature may be 5-20 °C cooler, the declining solubility of the sulfur in the solvent results in a sulfur liquid phase forming which is has higher specific gravity and settles from the anolyte. Then when the anolyte flows back toward the anodes where sulfur is forming through electrochemical oxidation of polysulfide, the anolyte has solubility has the capacity to dissolve the sulfur as it is formed, preventing fouling and polarization at the anodes or at membrane surfaces.

[0031] In one non-limiting embodiment within the scope of the ~~invention~~present disclosure, a cell for electrolyzing an alkali metal sulfide or polysulfide is provided where the cell operates at a temperature above the melting temperature of the alkali metal and where the cathode is wholly or partially immersed in a bath of the molten alkali metal with a divider between an anolyte compartment and a catholyte compartment. In this case the catholyte essentially comprises molten alkali metal but may also include solvent and alkali metal salt. The divider may be permeable to alkali metal cations and substantially impermeable to anions, solvent and dissolved sulfur. The divider comprises in part an alkali metal conductive ceramic or glass ceramic. The divider may be conductive to alkali ions which include lithium and sodium.

[0032] In another non-limiting embodiment, a cell for electrolyzing an alkali metal polysulfide is provided with an anolyte compartment and a catholyte compartment where the anolyte solution comprises a polar solvent and dissolved alkali metal polysulfide. The anolyte solution comprises a solvent that dissolves to some extent elemental sulfur. The anolyte may comprise a solvent where one or more of the solvents includes: *N,N*-dimethylaniline, quinoline, tetrahydrofuran, 2-methyl tetrahydrofuran, benzene,

tetrahydrofuran, benzene, cyclohexane, fluorobenzene, thrifluorobenzene, toluene, xylene, tetraethylene glycol dimethyl ether (tetraglyme), diglyme, isopropanol, ethyl propional, dimethyl carbonate, dimethoxy ether, dimethylpropyleneurea, formamide, methyl formamide, dimethyl formamide, acetamide, methyl acetamide, dimethyl acetamide, triethylamine, diethyl acetamide, ethanol and ethyl acetate, propylene carbonate, ethylene carbonate, and diethyl carbonate.

[0036] In one non-limiting embodiment, the anolyte solvent comprises from about 60-100 vol. % polar solvent and 0-40 vol. % apolar solvent. A blend of different anolyte solvents may help optimize the solubility of elemental sulfur and the solubility of sulfide and polysulfide.

[0037] Another non-limiting embodiment discloses a method for removal of dissolved elemental sulfur from a solvent/alkali metal polysulfide mixture includes cooling, reducing the solubility of sulfur in the solvent and causing a second liquid phase to form comprising elemental sulfur, and then separating the liquid phase sulfur from the liquid phase solvent mixture. The separation of liquid phase sulfur from liquid phase anolyte includes one or more of the following: gravimetric, centrifugation. The alkali metal polysulfide is of the class including sodium polysulfide and lithium polysulfide.

[0038] The present disclosure ~~invention~~ may provide certain advantages, including but not limited to the following:

[0039] Removing an alkali metal continuously or semi-continuously in liquid form from the cell.

[0040] Removing sulfur continuously or semi-continuously in liquid form from the cell.

[0041] Removing high alkali metal polysulfides and dissolved sulfur continuously or semi-continuously from the electrolytic cell, thereby reducing polarization of the anode by sulfur.

[0042] Separating sulfur continuously or semi-continuously from a stream containing a mixture of solvent, sulfur, and alkali metal polysulfides such that the solvent and alkali metal polysulfides are substantially recovered such that they can be returned back to an electrolytic process.

[0043] Operating the electrolytic cells at temperatures and pressures, so that the electrolytic cell materials of construction can include materials which would not tolerate high elevated temperature.

[0044] Reference throughout this specification to features, advantages, or similar language does not imply that all of the features and advantages that may be realized with the present

disclosure ~~invention~~ should be or are in any single embodiment of the disclosure~~invention~~. Rather, language referring to the features and advantages is understood to mean that a specific feature, advantage, or characteristic described in connection with an embodiment is included in at least one embodiment of the present disclosure~~invention~~. Thus, discussion of the features and advantages, and similar language, throughout this specification may, but do not necessarily, refer to the same embodiment, but may refer to every embodiment.

[0045] Furthermore, the described features, advantages, and characteristics of the present disclosure ~~invention~~ may be combined in any suitable manner in one or more embodiments. One skilled in the relevant art will recognize that the disclosure ~~invention~~ may be practiced without one or more of the specific features or advantages of a particular embodiment. In other instances, additional features and advantages may be recognized in certain embodiments that may not be present in all embodiments of the disclosure~~invention~~.

[0046] These features and advantages of the present disclosure ~~invention~~ will become more fully apparent from the following description and appended claims, or may be learned by the practice of the disclosure ~~invention~~ as set forth hereinafter.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0047] In order that the manner in which the above-recited and other features and advantages of the invention are obtained will be readily understood, a more particular description of the invention briefly described above will be rendered by reference to specific embodiments thereof that are illustrated in the appended drawings. Understanding that these drawings depict only typical embodiments of the invention and are not therefore to be considered to be limiting of its scope, the invention will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

[0048] Figure 1 shows an overall process for removing nitrogen, sulfur, and heavy metals from sulfur-, nitrogen-, and metal-bearing oil sources using an alkali metal and for regenerating the alkali metal.

[0049] Figures 2A and 2B show schematic processes for converting alkali metal hydrosulfide to alkali metal polysulfide and recovering hydrogen sulfide.

[0050] Figure 3 shows a schematic cross-section of an electrolytic cell which utilizes many of the features within the scope of the invention.

[0051] Figure 4 shows a schematic of several electrolytic cells operated in series to extract alkali metal and oxidize alkali metal sulfide to polysulfide and low polysulfide to high polysulfide and high polysulfide to sulfur.

CLAIMS:

1. An electrolytic cell for oxidizing alkali metal monosulfide or alkali metal polysulfides comprising:

an anolyte compartment configured with an anode and containing an anolyte solution comprising an alkali metal monosulfide, an alkali metal polysulfide, or a mixture thereof and an anolyte solvent that partially dissolves elemental sulfur, the anolyte compartment further comprising an anolyte solution inlet and an anolyte solution outlet;

a catholyte compartment configured with a cathode and containing a catholyte, wherein the catholyte comprises a molten alkali metal, the catholyte compartment further comprising a catholyte outlet;

an alkali ion conductive membrane configured to selectively transport alkali ions, wherein the alkali ion conductive membrane is substantially impermeable to anions, the anolyte solvent, and dissolved sulfur;

a source of electric potential electrically coupled to the anode and the cathode and configured to:

oxidize the alkali monosulfide or polysulfide in the anolyte compartment to form liquid elemental sulfur and alkali metal ions;

cause alkali metal ions to pass through the alkali ion conductive membrane from the anolyte compartment to the catholyte compartment; and

reduce the alkali metal ions in the catholyte compartment to form liquid elemental alkali metal;

an elemental sulfur settling zone where liquid elemental sulfur forms a second liquid phase and separates from the anolyte solution; and

a sulfur outlet for removal of the liquid elemental sulfur from the electrolytic cell disposed at a location lower than the anolyte solution outlet.

2. The electrolytic cell according to claim 1, wherein the alkali ion conductive membrane comprises in part an alkali metal conductive ceramic or glass ceramic.

3. The electrolytic cell according to claim 1, wherein the alkali ion conductive membrane comprises a solid MSICON (Metal Super Ion CONducting) material, where M is Na or Li.

4. The electrolytic cell according to claim 1, wherein the anolyte solvent comprises one or more solvents selected from N,N-dimethylaniline, quinoline, tetrahydrofuran, 2-methyl tetrahydrofuran, benzene, cyclohexane, fluorobenzene, thrifluorobenzene, toluene, xylene, tetraethylene glycol dimethyl ether (tetraglyme), diglyme, isopropanol, ethyl propional, dimethyl carbonate, dimethoxy ether, dimethylpropyleneurea, formamide, methyl formamide, dimethyl formamide, acetamide, methyl acetamide, dimethyl acetamide, triethylamine, diethyl acetamide, ethanol and ethyl acetate, propylene carbonate, ethylene carbonate, and diethyl carbonate.

5. The electrolytic cell according to claim 1, wherein the anolyte solvent comprises from about 60-100 vol. % polar solvent and 0-40 vol. % apolar solvent.

6. A plurality of coupled electrolytic cells comprising a first electrolytic cell according to claim 1 and a second electrolytic cell according to claim 1, wherein the anolyte solution inlet of the second electrolytic cell is connected to the anolyte solution outlet of the first electrolytic cell.

7. A plurality of coupled electrolytic cells comprising a first electrolytic cell according to claim 1, a second electrolytic cell according to claim 1, a third electrolytic cell according to claim 1, and a fourth electrolytic cell according to claim 1, wherein the anolyte solution inlet of the fourth electrolytic cell is connected to the anolyte solution outlet of the third electrolytic cell, wherein the anolyte solution inlet of the third electrolytic cell is connected to the anolyte solution outlet of the second electrolytic cell, and wherein the anolyte solution inlet of the second electrolytic cell is connected to the anolyte solution outlet of the first electrolytic cell.

CLAIMS:

1. A process for oxidizing alkali metal monosulfides and polysulfides electrochemically comprising:

obtaining an electrolytic cell comprising an alkali ion conductive membrane configured to selectively transport alkali ions, the membrane separating an anolyte compartment configured with an anode and a catholyte compartment configured with a cathode;

introducing into the anolyte compartment an anolyte solution comprising an alkali metal monosulfide, an alkali metal polysulfide, or a mixture thereof and an anolyte solvent that partially dissolves elemental sulfur;

introducing into the catholyte compartment a catholyte wherein the catholyte comprises a molten alkali metal;

applying an electric current to the electrolytic cell at an operating temperature thereby:

i. oxidizing monosulfide or polysulfide in the anolyte compartment to form liquid elemental sulfur;

ii. causing alkali metal ions to pass through the alkali ion conductive membrane from the anolyte compartment to the catholyte compartment; and

iii. reducing the alkali metal ions in the catholyte compartment to form liquid elemental alkali metal;

allowing liquid elemental sulfur to become saturated in the anolyte solution and to form a second liquid phase.

2. The process according to claim 1 where the liquid elemental sulfur separates from the anolyte solution in a settling zone that is within the electrolytic cell.

3. The process according to claim 1 where the liquid elemental sulfur separates from the anolyte solution in a settling zone that is external to the cell.

4. The process according to claim 1 where the separation of liquid elemental sulfur from the anolyte solution includes one or more of the separation techniques selected from gravimetric, filtration, and centrifugation.

5. The process according to claim 1, wherein the alkali ion conductive membrane is substantially impermeable to anions, the catholyte solvent, the anolyte solvent, and dissolved sulfur.

6. The process according to claim 1, wherein the alkali ion conductive membrane comprises in part an alkali metal conductive ceramic or glass ceramic.

7. The process according to claim 1, wherein the alkali ion conductive membrane comprises a solid MSICON (Metal Super Ion CONducting) material, where M is Na or Li.

8. The process according to claim 1, wherein the anolyte solvent comprises one or more solvents selected from N,N-dimethylaniline, quinoline, tetrahydrofuran, 2-methyl tetrahydrofuran, benzene, cyclohexane, fluorobenzene, thrifluorobenzene, toluene, xylene, tetraethylene glycol dimethyl ether (tetraglyme), diglyme, isopropanol, ethyl propional, dimethyl carbonate, dimethoxy ether, dimethylpropyleneurea, formamide, methyl formamide, dimethyl formamide, acetamide, methyl acetamide, dimethyl acetamide, triethylamine, diethyl acetamide, ethanol and ethyl acetate, propylene carbonate, ethylene carbonate, and diethyl carbonate.

9. The process according to claim 1, wherein the anolyte solvent comprises from about 60-100 vol. % polar solvent and 0-40 vol. % apolar solvent.

10. A process for oxidizing alkali metal polysulfides and monosulfides electrochemically comprising:

obtaining a first electrolytic cell comprising an alkali ion conductive membrane configured to selectively transport alkali ions, the membrane separating an anolyte compartment configured with an anode and a catholyte compartment configured with a cathode;

introducing into the anolyte compartment an anolyte solution comprising an alkali metal monosulfide, an alkali metal polysulfide, or a mixture thereof and an anolyte solvent that partially dissolves elemental sulfur;

introducing into the catholyte compartment a catholyte, wherein the catholyte comprises a molten alkali metal;

applying an electric current to the electrolytic cell thereby:

i. oxidizing sulfide or polysulfide in the anolyte compartment to form a higher level polysulfide;

ii. causing alkali metal ions to pass through the alkali ion conductive membrane from the anolyte compartment to the catholyte compartment; and

iii. reducing the alkali metal ions in the catholyte compartment to form elemental alkali metal;

transporting anolyte solution from the first electrolytic cell to a second electrolytic cell comprising an alkali ion conductive membrane configured to selectively transport alkali

ions, the membrane separating an anolyte compartment configured with an anode and a catholyte compartment configured with a cathode and a catholye;

applying an electric current to the second electrolytic cell thereby:

i. oxidizing polysulfide in the anolyte compartment to form liquid elemental sulfur;

ii. causing alkali metal ions to pass through the alkali ion conductive membrane from the anolyte compartment to the catholyte compartment; and

iii. reducing the alkali metal ions in the catholyte compartment to form liquid elemental alkali metal;

allowing liquid elemental sulfur to become saturated in the anolyte solution and to form a second liquid phase.

11. The process according to claim 10 where the liquid elemental sulfur separates from the anolyte solution in a settling zone that is within the electrolytic cell.

12. The process according to claim 10 where the liquid elemental sulfur separates from the anolyte solution in a settling zone that is external to the cell.

13. The process according to claim 10 where the separation of liquid elemental sulfur from the anolyte solution includes one or more of the separation techniques selected from gravimetric, filtration, and centrifugation.

14. The process according to claim 10, wherein the alkali ion conductive membrane is substantially impermeable to anions, the catholyte solvent, the anolyte solvent, and dissolved sulfur.

15. The process according to claim 10, wherein the alkali ion conductive membrane comprises in part an alkali metal conductive ceramic or glass ceramic.

16. The process according to claim 10, wherein the alkali ion conductive membrane comprises a solid MSICON (Metal Super Ion CONducting) material, where M is Na or Li.

17. The process according to claim 10, wherein the anolyte solvent comprises one or more solvents selected from N,N-dimethylaniline, quinoline, tetrahydrofuran, 2-methyl tetrahydrofuran, benzene, cyclohexane, fluorobenzene, thrifluorobenzene, toluene, xylene, tetraethylene glycol dimethyl ether (tetraglyme), diglyme, isopropanol, ethyl propional, dimethyl carbonate, dimethoxy ether, dimethylpropyleneurea, formamide, methyl formamide, dimethyl formamide, acetamide, methyl acetamide, dimethyl acetamide, triethylamine, diethyl acetamide, ethanol and ethyl acetate, propylene carbonate, ethylene carbonate, and diethyl carbonate.

18. The process according to claim 10, wherein the anolyte solvent comprises from about 60-100 vol. % polar solvent and 0-40 vol. % apolar solvent.

19. An electrolytic cell for oxidizing alkali metal polysulfides comprising:

an anolyte compartment configured with an anode and containing an anolyte solution comprising an alkali metal monosulfide, an alkali metal polysulfide, or a mixture thereof and an anolyte solvent that partially dissolves elemental sulfur, the anolyte compartment further comprising an anolyte solution inlet and an anolyte solution outlet;

a catholyte compartment configured with a cathode and containing a catholyte, wherein the catholyte comprises a molten alkali metal, the catholyte compartment further comprising a catholyte outlet;

an alkali ion conductive membrane configured to selectively transport alkali ions, wherein the alkali ion conductive membrane is substantially impermeable to anions, the anolyte solvent, and dissolved sulfur;

a source of electric potential electrically coupled to the anode and the cathode and configured to:

oxidize monosulfide or polysulfide in the anolyte compartment to form liquid elemental sulfur;

cause alkali metal ions to pass through the alkali ion conductive membrane from the anolyte compartment to the catholyte compartment; and

reduce the alkali metal ions in the catholyte compartment to form liquid elemental alkali metal; and

an elemental sulfur settling zone where liquid elemental sulfur separates from the anolyte solution.

20. The electrolytic cell according to claim 19, wherein the alkali ion conductive membrane comprises in part an alkali metal conductive ceramic or glass ceramic.

21. The electrolytic cell according to claim 19, wherein the alkali ion conductive membrane comprises a solid MSICON (Metal Super Ion CONducting) material, where M is Na or Li.

22. The electrolytic cell according to claim 19, wherein the anolyte solvent comprises one or more solvents selected from N,N-dimethylaniline, quinoline, tetrahydrofuran, 2-methyl tetrahydrofuran, benzene, cyclohexane, fluorobenzene, thrifluorobenzene, toluene, xylene, tetraethylene glycol dimethyl ether (tetraglyme), diglyme, isopropanol, ethyl propional, dimethyl carbonate, dimethoxy ether, dimethylpropyleneurea,

formamide, methyl formamide, dimethyl formamide, acetamide, methyl acetamide, dimethyl acetamide, triethylamine, diethyl acetamide, ethanol and ethyl acetate, propylene carbonate, ethylene carbonate, and diethyl carbonate.

23. The electrolytic cell according to claim 19, wherein the anolyte solvent comprises from about 60-100 vol. % polar solvent and 0-40 vol. % apolar solvent.

24. The electrolytic cell according to claim 19, further comprising a sulfur outlet for removal of elemental sulfur from the electrolytic cell.