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(54) **MERCURY REMOVAL PROCESS**

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(57) **ABSTRACT**

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A process is disclosed for decreasing the level of elemental mercury contained in a liquid hydrocarbon stream by a) contacting the liquid hydrocarbon stream with a water stream containing an oxidizing agent for conversion of at least a portion of the Hg(0) to Hg(II); b) extracting at least a portion of the Hg(II) from the liquid hydrocarbon stream into the water stream, thereby forming a treated liquid hydrocarbon stream and a waste water stream containing water and Hg(II); and c) separating the treated liquid hydrocarbon stream from the waste water stream.

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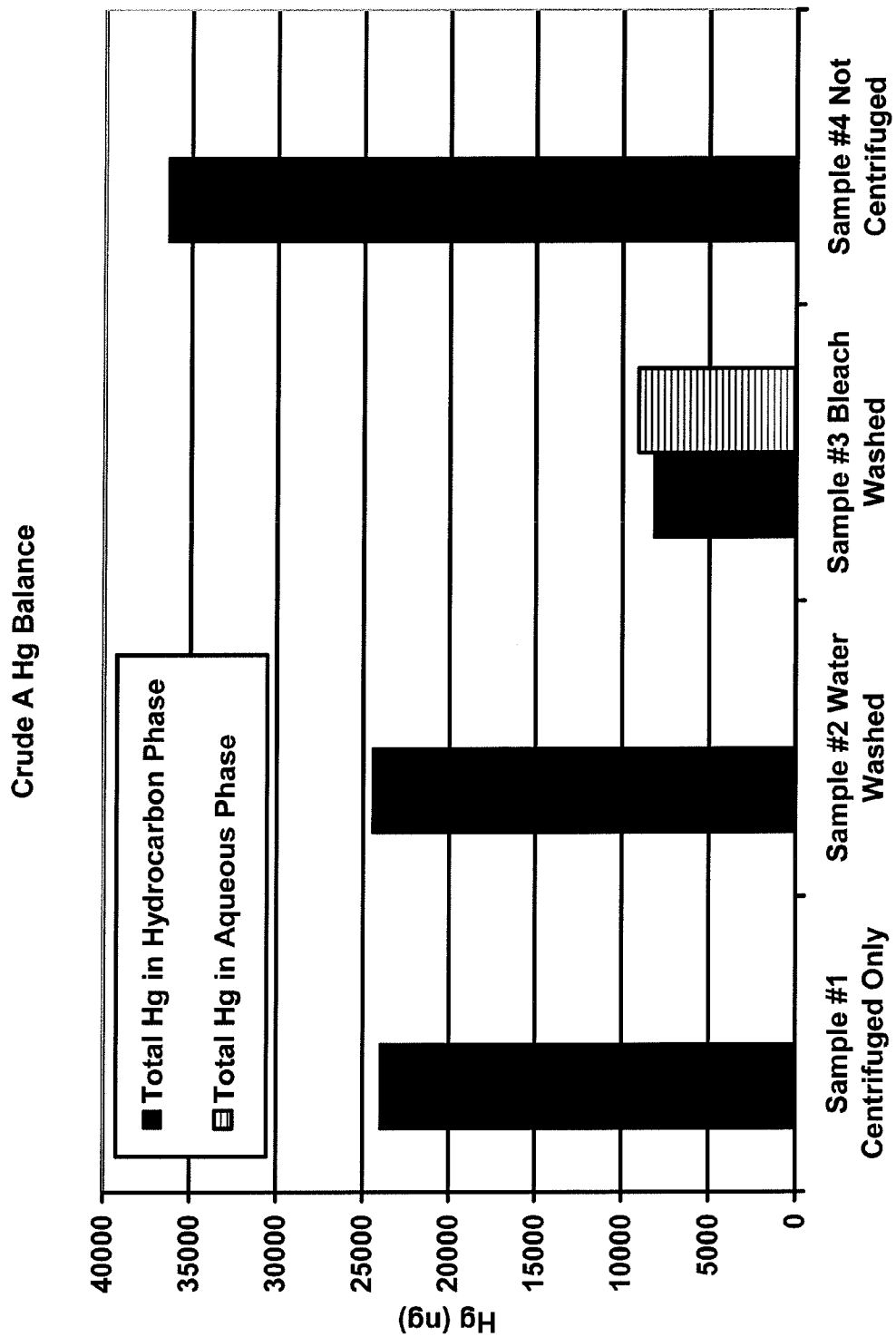


Figure 1

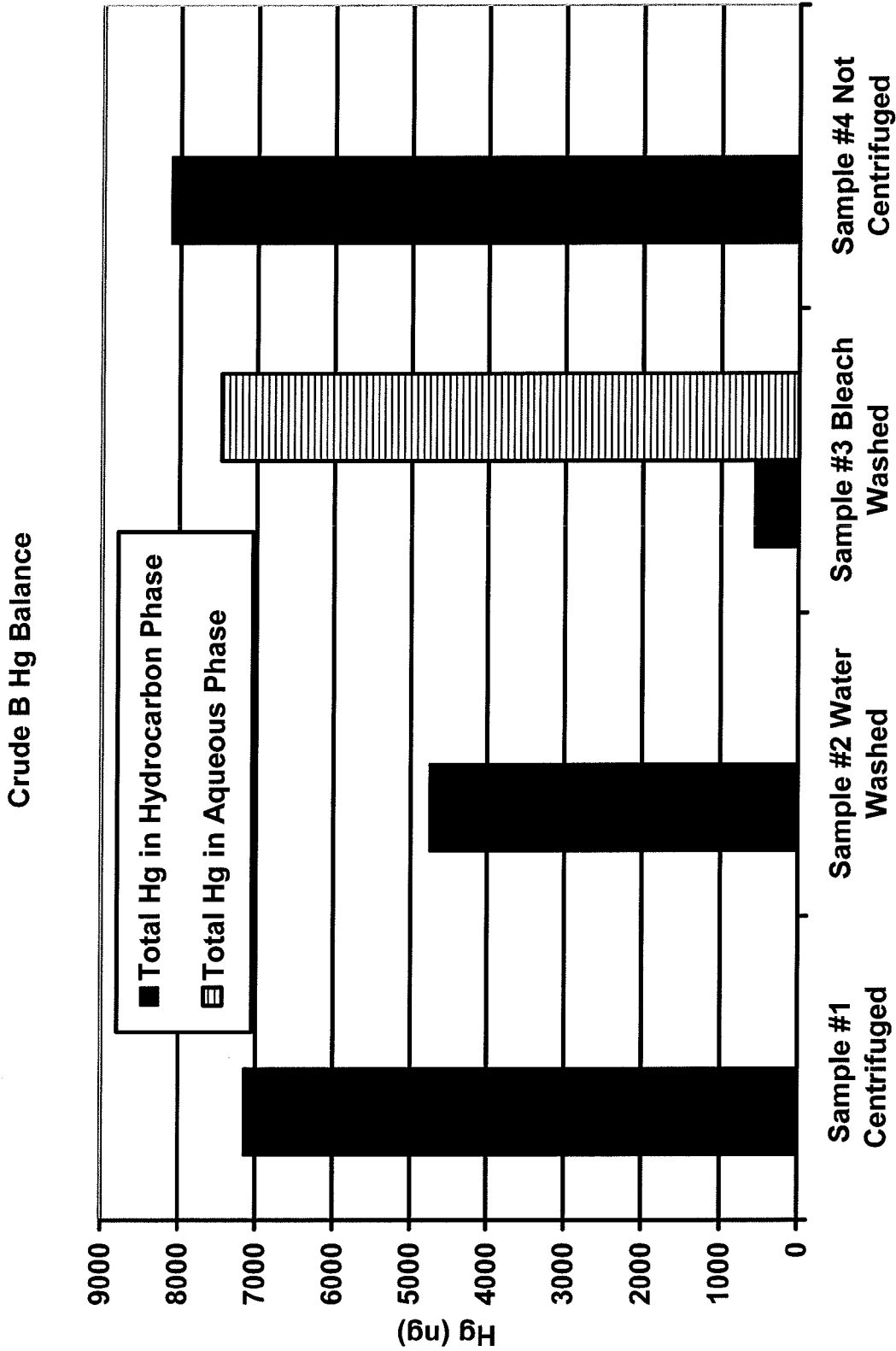


Figure 2

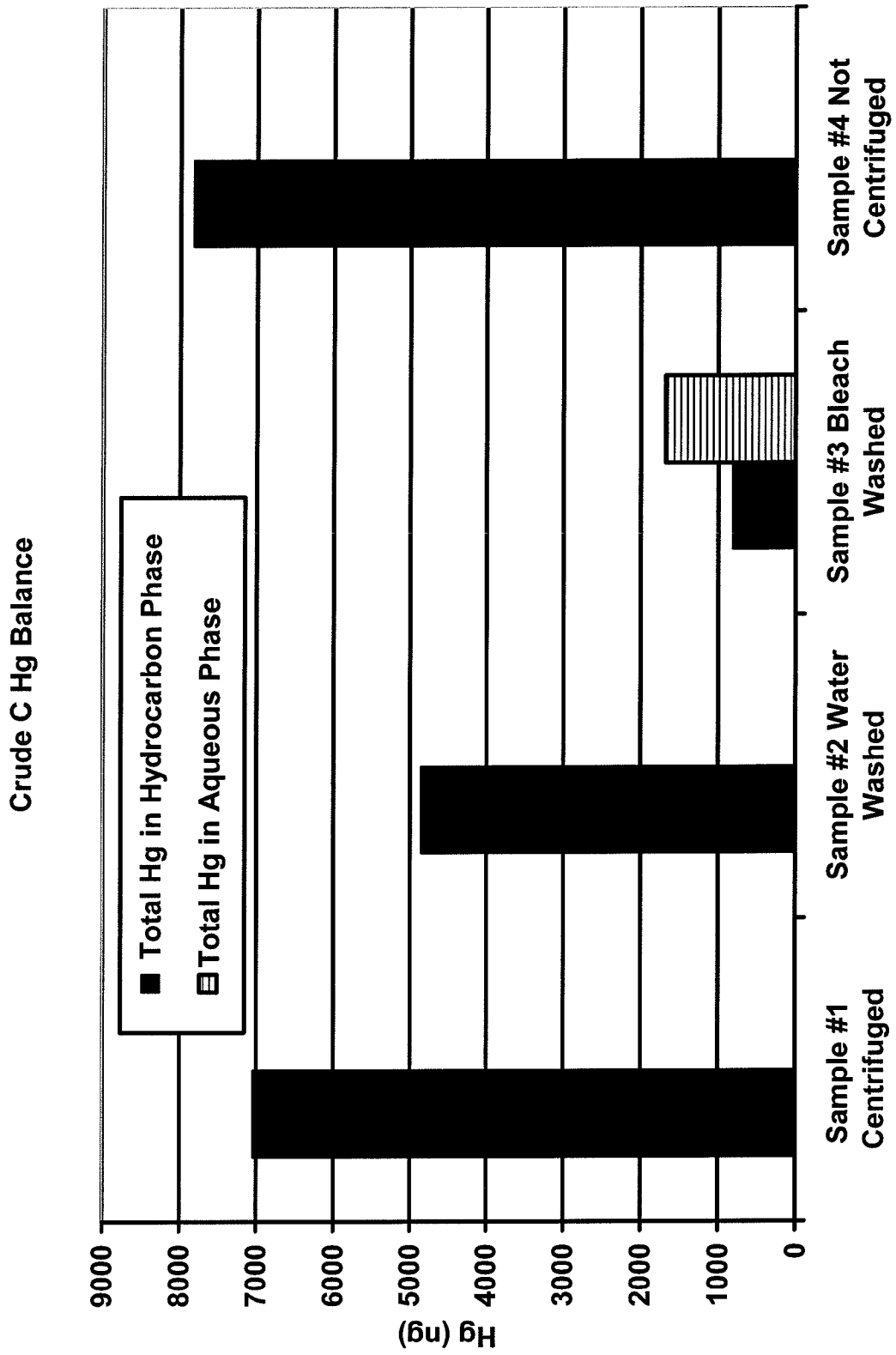


Figure 3

## MERCURY REMOVAL PROCESS

### FIELD OF THE INVENTION

[0001] The present invention relates to a process for the removal of mercury from crude oil. In another aspect, this invention relates to a process for the removal of mercury from crude oil using water and an oxidizing agent.

### BACKGROUND OF THE INVENTION

[0002] Since the presence of mercury in crude oil can cause problems with downstream processing units, as well as health and environmental concerns, there is an incentive to remove mercury from crude oil.

[0003] Therefore, development of an improved process for effectively removing mercury from crude oil before downstream processing into products would be a significant contribution to the art.

### BRIEF SUMMARY OF THE INVENTION

[0004] In accordance with the present invention, a process is provided including the following:

[0005] a) contacting a liquid hydrocarbon stream comprising liquid hydrocarbons and Hg(0) with a water stream consisting essentially of water and an oxidizing agent for conversion of at least a portion of the Hg(0) to Hg(II);

[0006] b) extracting at least a portion of the Hg(II) from the liquid hydrocarbon stream into the water stream, thereby forming a treated liquid hydrocarbon stream containing less total Hg than the liquid hydrocarbon stream and a waste water stream comprising water and Hg(II); and c) separating the treated liquid hydrocarbon stream from the waste water stream.

### BRIEF DESCRIPTION OF THE FIGURES

[0007] FIG. 1 is a bar graph showing the mass balance of Hg between the hydrocarbon and aqueous phases for variously treated samples of a crude oil.

[0008] FIG. 2 is a bar graph showing the mass balance of Hg between the hydrocarbon and aqueous phases for variously treated samples of a crude oil.

[0009] FIG. 3 is a bar graph showing the mass balance of Hg between the hydrocarbon and aqueous phases for variously treated samples of a crude oil.

### DETAILED DESCRIPTION OF THE INVENTION

[0010] The liquid hydrocarbon stream of this invention can be any liquid hydrocarbon stream which comprises liquid hydrocarbons and mercury in the 0 valence state (Hg (0)). Most typically, the liquid hydrocarbon stream will be a crude oil stream or a condensate stream from a natural gas well. Most typically the liquid hydrocarbon stream comprises, consists of, or consists essentially of a crude oil containing Hg(0).

[0011] The liquid hydrocarbon stream typically comprises at least about 10 ppb (parts per billion) Hg(0), and more particularly comprises at least about 200 ppb Hg (0).

[0012] The liquid hydrocarbon stream is contacted with a water stream consisting essentially of water and an oxidizing agent for conversion of at least a portion of the Hg(0) to mercury in a +2 valence state (Hg(II)). The oxidizing agent can be any chemical or chemical compound capable of oxidizing Hg(0) to Hg(II). The oxidizing agent can be sodium hypochlorite. The water stream preferably does not contain

any component(s) in sufficient quantities such that such component(s) materially affect the ability of the oxidizing agent to oxidize the Hg(0) to Hg(II) or materially affect the ability of the water to extract the Hg(II) from the liquid hydrocarbon stream.

[0013] The oxidizing agent is present in the water stream preferably in an amount such that the molar ratio of the oxidizing agent to the Hg(0) present in liquid hydrocarbon stream is at least about 1:1, more preferably at least about 7:1, and most preferably at least about 143:1.

[0014] The contacting of the liquid hydrocarbon stream with the water stream is preferably at a temperature at least above the freezing points of the liquid hydrocarbon stream and the water stream, more preferably at a temperature at least above the freezing points of the liquid hydrocarbon stream and the water stream and below about 100° C., and most preferably at a temperature at least above about 20° C. and below about 70° C.

[0015] At least a portion of the Hg(II) is then extracted from the liquid hydrocarbon stream into the water stream, thereby forming a treated liquid hydrocarbon stream containing less Hg than the liquid hydrocarbon stream and a waste water stream comprising water and Hg(II). The treated liquid hydrocarbon stream is then separated from the waste water stream by any suitable means.

[0016] The treated liquid hydrocarbon stream preferably contains less than about 50 wt. %, more preferably less than about 20 wt. %, and most preferably less than about 1 wt. %, of the Hg contained in the liquid hydrocarbon stream.

[0017] The following examples are provided to further illustrate this invention and are not to be considered as unduly limiting the scope of this invention.

### EXAMPLES

#### Example 1

[0018] To approximately 80 mL of decane, approximately 1 gram of Hg(0) was added. The mixture stirred for several days and the mercury spiked decane was decanted. Approximately 10 g of the spiked decane mixture was added to each of five 30 mL Nalgene® bottles. To the first bottle, nothing was added; to the second bottle, approximately 10 g of deionized water was added; to the third bottle, approximately 10 g of 5.6-6.0% bleach solution was added; to the fourth bottle, approximately 10 g of 5.6-6.0% bleach solution and 0.5 g of 4% hydrochloric acid solution was added; and to the fifth bottle, approximately 10 g of 4.6% sodium chloride solution was added.

[0019] All 5 bottles were shaken on a mechanical shaker for 30 minutes. A sample of the aqueous layer was removed via transfer pipette from bottles 2-5 for mercury analysis using the OhioLumex Cold Vapor Atomic Absorption Spectrometer (CVAA) coupled with the RP-91 attachment which utilizes chemical reduction of mercury via chemical reaction with stannous chloride. The organic layer (decane) was analyzed with the OhioLumex CVAA Spectrometer coupled with pyrolysis.

TABLE 1

<u>Partitioning of total mercury between decane and aqueous phases</u>		
Aqueous Additive	Percent Hg in Decane	Percent Hg in Aqueous
None	100%	N/A
DI Water	92%	8%
Bleach	0%	100%
Bleach + HCl	2%	98%
Sodium Chloride Soln.	90%	10%

[0020] Table 1 shows that compared to the first bottle with no aqueous wash, there was substantially more mercury removed from the hydrocarbon phase upon the addition of an oxidizing agent (bleach) to the aqueous wash.

## Example 2

[0021] Reagent grade decane, in the amounts shown in Table 2, was spiked with approximately 1.1 ppm of Hg(0) to which was added various quantities of 6 wt. % sodium hypochlorite solution and deionized water in the amounts shown in Table 2. The experiments were performed using the procedure outlined above in Example 1.

TABLE 2

<u>Assessing the minimum bleach needed to affect mercury removal</u>						
Decane Wt. (grams)	Bleach* Wt. (grams)	DI Water Wt. (grams)	Avg Hg(0) In Decane (ppb)	Wt. % NaOCl in Mixture	Mole Ratio Hg:NaOCl	% Total Hg Removal (Compared to Control)
10.15	0.00	0.00	1117	0	1:0	0%
10.50	10.00	0.00	5	2.93	1:143	99.6%
10.04	5.01	5.18	6	1.49	1:72	99.5%
10.15	1.03	9.02	33	0.31	1:15	97.0%
10.08	0.50	9.53	38	0.15	1:7	96.6%
10.08	0.11	10.13	231	0.03	1:2	79.3%

\*~6 wt. % stock NaOCl Soln.

[0022] As can be seen from Table 2, the optimal mole ratio of mercury to NaOCl in the decane/Bleach solution mix is at least about 1:7.

## Example 3

[0023] Samples of three different crude oils (designated as A, B and C) were heated beyond the wax point to obtain representative samples. For each crude oil, four samples of approximately 30 g each were prepared. To three of the four samples, the following bottles were prepared:

[0024] 1) crude oil only,

[0025] 2) crude oil and 3 g deionized water, and

[0026] 3) crude oil and 3 g of 5.6% to 6.0% sodium hypochlorite solution.

[0027] The fourth sample was capped and retained while the first three samples were shaken for 2 minutes. The three shaken samples were centrifuged at 70 degrees C. and 3500 RPM for 20 minutes to effect the separation. All hydrocarbon samples were analyzed for mercury using the OhioLumex CVAA coupled with pyrolysis. All aqueous samples were analyzed for mercury using the OhioLumex CVAA Spectrometer coupled with the RP-91 chemical reduction attachment.

[0028] FIGS. 1-3 are plots of the mass balance of mercury for samples 1-4 for crude oils A, B and C. The black bars in the graph represent the total mercury in ng of the analyzed hydrocarbon phase (or crude oil sample) and the grey bars (to the right of the black bars, if visible) represent the total mercury in ng of the analyzed aqueous phase. Errors due to loss of mass to a rag layer or dilution during centrifuge balancing were small and did not influence the conclusions drawn from the data.

[0029] It is clear that substantially more mercury was removed by the centrifuge separation for the bleach washed crude samples (the number 3 samples) as compared to the other samples, and the transfer of the mercury to the aqueous phase is evidenced by the increase in mercury concentration in the aqueous layer, as is depicted in the Figures.

## Example 4

[0030] A sample of a crude oil was heated beyond the wax point to obtain a representative sample. To four glass bottles, the following was added: 1) 40 g crude oil only, 2) 40 g crude oil and 4 g deionized water, 3) 40 g crude oil and 4 g 5.6-6.0% sodium hypochlorite (bleach) solution, and 4) 40 g crude oil and 4 g 50% ethylene glycol in water solution. The four samples were shaken for 2 minutes. The four shaken samples were centrifuged at 90 degrees C. and 3500 RPM for 20 minutes to effect the separation. All hydrocarbon samples and the sample of ethylene glycol/water were analyzed for mercury using the OhioLumex CVAA coupled with pyrolysis. All aqueous samples were analyzed for mercury using the OhioLumex CVAA Spectrometer coupled with the RP-91 chemical reduction attachment. Results are shown in Table 3 below, and show that the addition of bleach had a significant effect on Hg removal from the crude as compared to the use of ethylene glycol or DI water to wash the crude.

TABLE 3

	Avg. Hg in Crude (ng)	Avg. Hg in Aqueous (ng)	% Hg in Crude	% Hg in Aqueous
Control	22663	0	100%	0%
Ethylene Glycol	21384	64	100%	0%
DI Water	22490	20	100%	0%
Bleach	5868	13683	30%	70%

[0031] While this invention has been described in detail for the purpose of illustration, it should not be construed as limited thereby but intended to cover all changes and modifications within the spirit and scope thereof.

That which is claimed:

1. A process comprising:

- contacting a liquid hydrocarbon stream comprising liquid hydrocarbons and Hg(0) with a water stream consisting essentially of water and an oxidizing agent for conversion of at least a portion of said Hg(0) to Hg(II);
- extracting at least a portion of said Hg(II) from said liquid hydrocarbon stream into said water stream, thereby forming a treated liquid hydrocarbon stream containing less Hg than said liquid hydrocarbon stream and a waste water stream comprising water and Hg(II); and
- separating said treated liquid hydrocarbon stream from said waste water stream.

2. A process in accordance with claim 1 wherein said liquid hydrocarbon stream comprises crude oil and Hg (0).

3. A process in accordance with claim 1 wherein said oxidizing agent is sodium hypochlorite.

4. A process in accordance with claim 1 wherein said oxidizing agent is present in said water stream in an amount such that the molar ratio of said oxidizing agent to said Hg(0) present in said liquid hydrocarbon stream is at least about 1:1.

5. A process in accordance with claim 1 wherein said oxidizing agent is present in said water stream in an amount such that the molar ratio of said oxidizing agent to said Hg(0) present in said liquid hydrocarbon stream is at least about 7:1.

6. A process in accordance with claim 1 wherein said oxidizing agent is present in said water stream in an amount such that the molar ratio of said oxidizing agent to said Hg(0) present in said liquid hydrocarbon stream is at least about 143:1.

7. A process in accordance with claim 1 wherein said contacting of said liquid hydrocarbon stream with said water stream is at a temperature at least above the freezing points of said liquid hydrocarbon stream and said water stream.

8. A process in accordance with claim 1 wherein said contacting of said liquid hydrocarbon stream with said water

stream is at a temperature at least above the freezing points of said liquid hydrocarbon stream and said water stream and below about 100° C.

9. A process in accordance with claim 1 wherein said contacting of said liquid hydrocarbon stream with said water stream is at a temperature at least above about 20° C. and below about 70° C.

10. A process in accordance with claim 1 wherein said treated liquid hydrocarbon stream contains less than about 50 wt. % of the total Hg contained in said liquid hydrocarbon stream.

11. A process in accordance with claim 1 wherein said treated liquid hydrocarbon stream contains less than about 20 wt. % of the total Hg contained in said liquid hydrocarbon stream.

12. A process in accordance with claim 1 wherein said treated liquid hydrocarbon stream contains less than about 1 wt. % of the total Hg contained in said liquid hydrocarbon stream.

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