operator needs to measure the pH of the solution before it travels into and through the vessel to be treated as compared to the pH measurement afterward. To obtain that comparative measurement, the operator must circulate within a closed loop. Moreover, this measurement and testing need precludes even the thought of a once-through application.

SUMMARY

[0013a] In one aspect, there is provided a method of removal metal sulfides from a spent catalyst located within a reactor vessel, the method comprising:

a) purging a reactor vessel containing a spent catalyst;

b) bringing the reactor vessel to a first operating temperature;

c) injecting an oxidizing agent formulation into the reactor vessel;

d) subjecting the reactor vessel to a dry gas purge;

e) bringing the reactor vessel temperature to a second operating temperature; and

f) isolating the reactor vessel from external contaminant sources and introducing air into the reactor vessel.

[0013b] In another aspect, there is provided a method of removal metal sulfides from a spent catalyst located within a reactor vessel, the method comprising:

a) purging a reactor vessel containing a spent catalyst;

b) bringing the reactor vessel to a first operating temperature;

c) partially or completely filling the reactor vessel with an oxidizing agent formulation;

d) removing remaining oxidizing agent formulation from the reactor vessel;

e) subjecting the reactor vessel to a first inert gas purge;

f) bringing the reactor vessel to a second operating temperature while subjecting the reactor vessel to a second inert gas purge;

g) bringing the reactor vessel to a third operating temperature; and

h) isolating the reactor vessel from external contaminant sources and introducing air into the reactor vessel.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is a schematic flowchart of a method for removing metal sulfides from a catalyst bed in a reactor vessel and removal of sulfides and halides in a reactor system within which the reactor vessel is integrated in accordance with various aspects of the disclosure;

[0015] FIG. 2 is a schematic flowchart of another method for removing metal sulfides from a catalyst bed in a reactor vessel and removal of sulfides and halides in a reactor system within which the reactor vessel is integrated in accordance with various aspects of the disclosure;

[0016] FIG. 3 is an image of an exemplary laboratory scale system for removing metal sulfides from a spent catalyst material in accordance with various aspects of the disclosure;

[0017] FIGS. 4A-G are graphs showing data obtained from treating a spent catalyst material, in the laboratory scale system of FIG. 3, with water and subsequently subjecting it to a hot air purge in accordance with various aspects of the disclosure;

[0018] FIGS. 5A-E are graphs showing subsets of the data of FIG. 4A-D and 4G;

[0019] FIGS. 6A-G are graphs showing data obtained from treating a spent catalyst material, in the laboratory scale system of FIG. 3, with an aqueous solution comprising 5 wt% $NaNO_2$, 1 wt% LDAO and 1 wt% Na_2HPO_4 and subsequently subjecting it to a hot air purge in accordance with various aspects of the disclosure;

[0020] FIGS. 7A-D are graphs showing subsets of the data of FIGS. 6D-G;

[0021] FIGS. 8A-G are graphs showing other subsets of the data of FIGS. 6A-G;

[0022] FIGS. 9A-E are graphs showing data obtained from treating a spent catalyst material, in the laboratory scale system of FIG. 3, with an aqueous solution comprising 10 wt% $NaNO_2$ and subsequently subjecting it to a hot air purge in accordance with various aspects of the disclosure;

[0023] FIGS. 10A-D are graphs showing subsets of the data of FIGS. 9B-E;

[0024] FIGS. 11A-E are graphs showing data obtained from treating a spent catalyst material, in the laboratory scale system of FIG. 3, with an aqueous solution comprising 10 wt% $NaNO_2$, 0.8 wt% LDAO and 0.8 wt% Na_2HPO_4 and subsequently subjecting it to a hot air purge in accordance with various aspects of the disclosure;

CLAIMS

What is claimed is:

1. A method of removal metal sulfides from a spent catalyst located within a reactor vessel, the method comprising:

a) purging a reactor vessel containing a spent catalyst;

b) bringing the reactor vessel to a first operating temperature;

c) injecting an oxidizing agent formulation into the reactor vessel;

d) subjecting the reactor vessel to a dry gas purge;

e) bringing the reactor vessel temperature to a second operating temperature; and

f) isolating the reactor vessel from external contaminant sources and introducing air into the reactor vessel.

~~2. The method of claim 1, further comprising, entering the reactor vessel to recover remaining spent catalyst, the remaining spent catalyst comprising metal oxide reaction products.~~

~~3~~2. The method of claim 1~~ or 2~~, further comprising monitoring the oxygen content of off-gases expelled from the reactor vessel during the first dry gas purge.

~~4~~3. The method of ~~any one of~~ claim~~s~~ 1~~-3~~, wherein the oxidizing agent formulation is injected into the reactor vessel continuously, incrementally ~~of~~ or variably over a predetermined period of time.

~~5~~4. The method of any one of claims 1-~~4~~3, wherein the oxidizing agent formulation comprises one or more oxidizing agents.

~~6~~5. The method of any one of claims 1-~~5~~3, wherein the oxidizing agent formulation comprises a pH buffer.

~~7~~6. The method of any one of claims 1-~~6~~3, wherein the oxidizing agent formulation comprises one or more water-soluble organic solvents and/or one or more water-soluble surfactants.

~~8~~7. The method of any one of claims 1-~~7~~3, wherein injecting the oxidizing agent formulation into the reactor vessel while maintaining the reactor vessel at the first operating temperature further comprises monitoring off-gases expelled from the reactor vessel H_2S and SO_2.

~~9~~8. The method of any one of claims 1-~~9~~3, wherein subjecting the reactor vessel to the dry gas purge further comprises removing liquid from the reactor vessel and drying the contents of the reactor vessel.

~~10~~9. The method of any one of claims 1-~~9~~3, wherein the metal sulfides comprise one or more of nickel sulfides, molybdenum sulfides, cobalt sulfides, iron sulfides, copper sulfides, tungsten sulfides, titanium sulfides, manganese sulfides, chromium sulfides, noble metal promoted-molybdenum sulfides, non-noble metal promoted-molybdenum sulfides, zinc sulfides, and lead sulfides.

~~11~~10. The method of any one of claims 1-~~10~~3, wherein the oxidizing agent formulation comprises sodium nitrite.

~~12. The method of claim 11, wherein the oxidizing agent formulation further comprises lauryldimethylamine oxide (LDAO).~~

~~13~~11. The method of any one of claims 1-~~10~~3, wherein the oxidizing agent formulation comprises lauryldimethylamine oxide (LDAO).

~~14~~12. The method of any one of claims 1-~~13~~3, wherein the oxidizing agent formulation has a pH ranging from about 7 to about 9.5.

~~15. The method of any one of claims 1-14, wherein the spent catalyst is a spent NiMo hydroprocessing catalyst.~~

~~16~~13. The method of any one of claims 1-~~15~~3, wherein c) injecting the oxidizing agent formulation into the reactor vessel is performed while maintaining the reactor vessel at the first operating temperature.

~~17~~14. The method of any one of claims 1-~~15~~3, wherein a) purging the reactor vessel containing the spent catalyst is performed with a dry gas, steam or water.

~~18~~15. The method of any one of claims 1-~~17~~3, further comprising injecting a pH buffering solution into the reaction vessel between steps c) and d).

~~19~~16. A method of removal metal sulfides from a spent catalyst located within a reactor vessel, the method comprising:

a) purging a reactor vessel containing a spent catalyst;

b) bringing the reactor vessel to a first operating temperature;

c) partially or completely filling the reactor vessel with an oxidizing agent formulation;

d) removing remaining oxidizing agent formulation from the reactor vessel;

e) subjecting the reactor vessel to a first inert gas purge;

f) bringing the reactor vessel to a second operating temperature while subjecting the reactor vessel to a second inert gas purge;

g) bringing the reactor vessel to a third operating temperature; and

h) isolating the reactor vessel from external contaminant sources and introducing air into the reactor vessel.

~~20. The method of claim 19, further comprising, entering the reactor vessel to recover remaining spent catalyst, the remaining spent catalyst comprising metal oxide reaction products.~~

~~21~~17. The method of claim ~~19 or 20~~16, further comprising monitoring the oxygen content of off-gases expelled from the reactor vessel during the ~~dry~~ first or second inert gas purge.

~~22~~18. The method of ~~any one of~~ claim~~s~~ ~~19-21~~16, wherein after the reactor vessel has been partially or completely filled with the oxidizing agent formulation, the oxidizing agent formulation is maintained or circulated within the reactor vessel for a period of time.

~~23. The method of any one of claims 19-22, wherein the oxidizing agent formulation comprises one or more oxidizing agents.~~

~~24. The method of any one of claims 19-23, wherein the oxidizing agent formulation comprises a pH buffer.~~

~~25. The method of any one of claims 19-24, wherein the oxidizing agent formulation comprises one or more water-soluble organic solvents and/or one or more water-soluble surfactants.~~

~~26~~19. The method of ~~any one of~~ claim~~s 19-25~~16, wherein subjecting the reactor vessel to the first inert gas purge further comprises monitoring off-gases expelled from the reactor vessel H_2S and SO_2.

~~27~~20. The method of ~~any one of~~ claim~~s 19-26~~16, wherein subjecting the reactor vessel to the second inert gas purge further comprises removing liquid from the reactor vessel and drying the contents of the reactor vessel.

~~28. The method of any one of claims 19-27, wherein the metal sulfides comprise one or more of nickel sulfides, molybdenum sulfides, cobalt sulfides, iron sulfides, copper sulfides, tungsten sulfides, titanium sulfides, manganese sulfides, chromium sulfides, noble metal promoted-molybdenum sulfides, non-noble metal promoted-molybdenum sulfides, zinc sulfides, and lead sulfides.~~

~~29. The method of any one of claims 19-28, wherein the oxidizing agent formulation comprises sodium nitrite.~~

~~30. The method of claim 29, wherein the oxidizing agent formulation further comprises lauryldimethylamine oxide (LDAO).~~

~~31. The method of any one of claims 19-28, wherein the aqueous oxidizing agent solution comprises lauryldimethylamine oxide (LDAO).~~

~~32. The method of any one of claims 19-31, wherein the oxidizing agent formulation has a pH ranging from about 7 to about 9.5.~~

~~33. The method of any one of claims 19-32, wherein the spent catalyst is a spent NiMo hydroprocessing catalyst.~~

~~34~~21. The method of any one of claims ~~19~~16-~~33~~20, wherein c) partially or completely filling the reactor vessel with an oxidizing agent formulation is performed while maintaining the reactor vessel at the first operating temperature.

~~35. The method of any one of claims 1-15, wherein a) purging the reactor vessel containing the spent catalyst is performed with a dry gas, steam or water.~~

~~36~~22. The method of any one of claims ~~19~~16-~~35~~20, further comprising injecting a pH buffering solution into the reaction vessel between step f) and step g).

~~37~~23. The method of any one of claims 1~~-18 and 35~~ to 3, wherein the method further eliminates formation of polythionic and thionic acids, and/or eliminates formation of halide acids in piping and/or components of a reactor system comprising the reactor vessel.

~~37~~24. The method of any one of claims ~~19-34 and 36~~16 to 20, wherein the method further eliminates formation of polythionic and thionic acids, and/or eliminates formation of halide acids in piping and/or components of a reactor system comprising the reactor vessel.