chromatographic columns or packed-bed columns/reactors. In this manner, an intermediate liquid stream comprising lithium (Li) and one or more recovered products comprising one or more of nickel (Ni), manganese (Mn), and cobalt (Co) is generated. The one or more recovered products are removed from the intermediate liquid stream. The process also comprises introducing the intermediate liquid stream into a lithium precipitation reactor to precipitate at least one compound comprising lithium (Li).

[0009] In one example, the purifying may include precipitating copper (Cu) via a cementation reaction or a sulfidation reaction.

[0010] In one example, the removing copper (Cu) from the waste liquid stream comprises precipitating copper (Cu) by adding a source of iron (Fe) and a second inorganic base to the waste liquid stream to precipitate copper (Cu) via a cementation reaction.

[0011] In one further example, the source of iron (Fe) comprises iron powder, the first inorganic base and the second inorganic base each comprise sodium hydroxide (NaOH), the source of calcium oxide is selected from the group consisting of: lime (CaO), calcium hydroxide ($Ca(OH)_2$), and combinations thereof, and the oxidant is selected from the group consisting of: hydrogen peroxide (H_2O_2), ozone (O_3), sodium hypochlorite (NaClO), and combinations thereof.

[0012] In one further example, the second inorganic base is added until pH is about 5, the first organic base is added until pH is about 10.5, and the oxidant comprises hydrogen peroxide (H_2O_2) which is added at a concentration of greater than or equal to about 4 % by volume to less than or equal to about 6% by volume of total liquid contents (waste liquid stream).

[0013] In one further example, the adding the source of iron (Fe) and the second inorganic base to the waste liquid stream is conducted at a pH of greater than or equal to about 1 to less than or equal to about 2 while mixing for a duration of greater than or equal to about 15 minutes at a temperature of greater than or equal to about 55°C to less than or equal to about 65°C.

[0014] In one further example, about 2.5 g of iron powder is added for each liter (L) of the waste liquid stream.

[0015] In one example, the removing copper (Cu) from the waste liquid stream comprises precipitating copper (Cu) by adding a source of sodium sulfide (Na_2S) to the waste liquid stream to precipitate copper (Cu) via a sulfidation reaction.

[0016] In one example, the removing copper (Cu) from the waste liquid stream comprises subjecting the waste liquid stream to a solvent-extraction process by mixing the waste liquid stream with an extractant and an organic phase to remove copper (Cu).

[0017] In one further example, the extractant comprises 2-hydroxy-5-nonylbenzaldehyde oxime and the organic phase comprises kerosene.

[0018] In one further example, the solvent-extraction process further removes iron (Fe) from the waste liquid stream.

[0019] In one example, the purifying further includes introducing a source of phosphate to the waste liquid stream prior to the (iii) adding the first inorganic base to increase pH of the waste liquid stream so as to generate aluminum phosphate ($AlPO_4$) precipitate.

[0020] In one further example, the source of phosphate comprises sodium phosphate (Na_3PO_4).

[0021] In one example, the adding the source of calcium oxide and the oxidant to generate calcium fluoride (CaF_2) is conducted at a pH of greater than or equal to about 1 to less than or equal to about 2 while mixing for a duration of greater than or equal to about 30 minutes at a temperature of greater than or equal to about 55°C to less than or equal to about 65°C.

[0022] In one example, the adding of the first inorganic base increases the pH of the waste liquid stream to greater than or equal to about 4 to less than or equal to about 5.

[0023] In one example, the adding of the first inorganic base to increase pH is conducted while mixing for a duration of greater than or equal to about 60 minutes at a temperature of greater than or equal to about 55°C to less than or equal to about 65°C.

[0024] In one example, the purified filtrate liquid stream comprises nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) and the separating nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate liquid stream occurs by passing the purified filtrate liquid stream into the second reactor. In the second reactor, the co-precipitation process is conducted that comprises increasing the pH of the purified filtrate liquid stream to greater than or equal to about 11 in an inert environment to form nickel hydroxide hydrate ($Ni(OH)_2 \cdot 6H_2O$), manganese hydroxide hydrate ($Mn(OH)_2 \cdot H_2O$), and cobalt hydroxide hydrate ($Co(OH)_2 \cdot 7H_2O$) that concurrently precipitate from the purified filtrate liquid stream to generate the one or more recovered products.

[0025] In one further example, the increasing the pH of the purified filtrate liquid stream further comprises first adding ammonia to the purified liquid stream that comprises nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$).

[0026] In one example, the one or more recovered products is an electroactive material precursor having a stoichiometry of $Ni_xMn_yCo_{1-x-y}(OH)_2$, where x is < 1 and y is < 1.

[0027] In one example, the one or more recovered products has a stoichiometry of about $\frac{1}{3}Ni(OH)_2 + \frac{1}{3}Mn(OH)_2 + \frac{1}{3}Co(OH)_2 \rightarrow Ni_{0.33}Mn_{0.33}Co_{0.33}(OH)_2$.

[0028] In one example, the process further comprises determining a first ratio of Ni:Mn:Co in the purified filtrate liquid stream prior to the co-precipitation process. The first ratio is then compared to a target stoichiometric ratio of Ni:Mn:Co for the one or more recovered products. The, the process may include adding one of more of nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) to the purified filtrate liquid stream to adjust an amount of nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) prior to adjusting the pH. In this manner, the one or more recovered products has a second ratio corresponding to the target stoichiometric ratio.

[0029] In one example, the separating occurs by passing the purified filtrate liquid stream in a first direction in a chromatographic column or packed-bed column/reactor comprising a chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 4.5 that generates a raffinate stream comprising at least one manganese (Mn)-containing species and at least one lithium (Li)-containing species that exits the packed-bed column/reactor, while nickel (Ni) ions and cobalt (Co) ions are retained on the chelating resin in the packed-bed column/reactor. The process further includes regenerating the packed-bed column/reactor by passing a regeneration liquid having a pH of less than or equal to about 1.5 in the packed-bed column/reactor to form an extract stream comprising the nickel (Ni) ions and cobalt (Co) ions. The process also

includes precipitating nickel hydroxide ($Ni(OH)_2$) and cobalt hydroxide ($Co(OH)_2$) from the extract.

[0030] In one example, the method further comprises forming a precursor of $LiNiCoAlO_2$ electroactive material by combining the nickel hydroxide ($Ni(OH)_2$) and cobalt hydroxide ($Co(OH)_2$) with the aluminum hydroxide ($Al(OH)_3$) and at least one compound comprising lithium (Li).

[0031] In certain examples, manganese in the raffinate stream/purified filtrate liquid stream may be precipitated, for example, as a manganese oxide (*e.g.*, manganese dioxide MnO_2) or manganese hydroxide ($Mn(OH)_2$). In one variation, the manganese removal via precipitation to form manganese oxide (*e.g.*, manganese dioxide (MnO_2)) may be achieved by conducting one or more of the following processes: by adding sodium permanganate, potassium permanganate, or by subjecting the raffinate to an ozonation process. In certain examples, a combination of these manganese removal processes provides maximum manganese precipitation levels.

[0032] In another variation, the process may further comprise adjusting the pH of the purified filtrate liquid stream to be greater than or equal to about 4 to less than or equal to about 5 as it enters the packed-bed column/reactor. The process further comprises precipitating manganese hydroxide ($Mn(OH)_2$) by adjusting pH to be greater than or equal to about 8 to less than or equal to about 10 and separating the manganese hydroxide ($Mn(OH)_2$).

[0033] In one example, the at least one compound comprising lithium (Li) comprises lithium carbonate (Li_2CO_3) that is combined with manganese hydroxide ($Mn(OH)_2$) to form $LiMnO_4$ electroactive material.

[0034] In one example, the adjusting the pH comprises adding sodium hydroxide (NaOH) to the purified filtrate liquid stream.

[0035] In one example, a stationary phase in the packed-bed column/reactor comprises a macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid.

[0036] In one example, the separating occurs by passing the purified filtrate liquid stream in a first direction in a first packed-bed column/reactor comprising a first chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 1.5. This generates a first raffinate stream comprising at least one manganese (Mn)-containing species, at least one cobalt (Co)-containing species, and at least one lithium (Li)-containing species that exits the first packed-bed column/reactor, while nickel (Ni) ions are retained on the first chelating resin in the first packed-bed column/reactor. The process also comprises passing the first raffinate stream in a first direction in a second packed-bed column/reactor comprising a second chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 2.5 that generates a second raffinate stream comprising at least one manganese (Mn)-containing species and at least one lithium (Li)-containing species that exits the second packed-bed column/reactor, while cobalt (Co) ions are retained on the second chelating resin in the second packed-bed column/reactor. The process further comprises regenerating the first packed-bed column/reactor by passing a first regeneration liquid having a pH of less than or equal to about 1.5 in the first packed-bed column/reactor to form a first extract stream comprising the nickel (Ni) ions. Next, nickel hydroxide ($Ni(OH)_2$) may be precipitated from the first extract stream. The process also includes regenerating the second packed-

bed column/reactor by passing a second regeneration liquid having a pH of less than or equal to about 2.5 in the second packed-bed column/reactor to form a second extract stream comprising the cobalt (Co) ions. This is followed by precipitating cobalt hydroxide ($Co(OH)_2$) from the second extract stream.

[0037] In one example, the process further comprises forming a precursor of $LiNiCoAlO_2$ electroactive material by combining the nickel hydroxide ($Ni(OH)_2$) and cobalt hydroxide ($Co(OH)_2$) with the aluminum hydroxide ($Al(OH)_3$) and the at least one compound comprising lithium (Li).

[0038] In one example, the process further comprises precipitating manganese hydroxide ($Mn(OH)_2$) from the second raffinate stream by adjusting pH to be greater than or equal to about 8 to less than or equal to about 10 thus forming the intermediate liquid stream. The manganese hydroxide ($Mn(OH)_2$) is then separated from the intermediate liquid stream.

[0039] In one example, the at least one compound comprising lithium (Li) comprises lithium carbonate (Li_2CO_3) that is combined with manganese hydroxide ($Mn(OH)_2$) to form $LiMnO_4$ electroactive material.

[0040] In one example, the process further comprises adjusting the pH of the purified filtrate liquid stream by adding sodium hydroxide (NaOH) to the purified filtrate liquid stream to have a pH of about 2.5 and adjusting the pH of the first raffinate stream by adding sodium hydroxide (NaOH) to the first raffinate stream to have a pH of about 3.5.

[0041] In one example, a stationary phase in the first packed-bed column/reactor comprises macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid and a stationary phase in the second packed-bed column/reactor

comprises macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid.

[0042] In one example, the lithium-ion battery waste stream is black mass. Prior to the purifying, the method further comprises generating the lithium-ion battery waste liquid stream by subjecting the black mass to a leaching process that comprises mixing an inorganic acid with the black mass to form an acidic admixture. An oxidant may be mixed with the acidic admixture. The process may further include adding deionized water to the acidic admixture. Then, a leachate stream is passed through a second filter to generate a filtrate liquid stream comprising one or more metal sulfates and a first retentate comprising graphite.

[0043] In one further example, both the mixing of the inorganic acid and the mixing of the oxidant are conducted at a temperature of less than or equal to about 100°C.

[0044] In one further example, the inorganic acid comprises sulfuric acid (H_2SO_4), the oxidant comprises hydrogen peroxide (H_2O_2), and a pH of the acidic admixture is less than or equal to about 2.5.

[0045] In one further example, the mixing the inorganic acid comprises adding black mass to the sulfuric acid (H_2SO_4) having a molarity of about 4M, the mixing the oxidant comprises adding about 30% by mass hydrogen peroxide (H_2O_2) to the acidic admixture so that the acidic admixture has a solid/liquid ratio of 100 g/L, followed by mixing for greater than or equal to about 2 hours, and then the adding of the deionized water dilutes the sulfuric acid (H_2SO_4) to a molarity of about 2M, followed by mixing for greater than or equal to about 30 minutes.

[0046] In one example, the one or more recovered products has a purity level of greater than or equal to about 95% and comprises less than or equal to about 5% by mass of a total cumulative amount of impurities comprising aluminum (Al), copper (Cu), iron (Fe), phosphorus (P), titanium (Ti) and fluorine (F).

[0047] In one example, the one or more recovered products has a purity level of greater than or equal to about 98% and comprises less than or equal to about 2% by mass of a total cumulative amount of impurities comprising aluminum (Al), copper (Cu), iron (Fe), phosphorus (P), titanium (Ti) and fluorine (F).

[0048] In one example, the separating recovers greater than or equal to about 80% by mass of each of nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate liquid stream.

[0049] In one example, prior to the separating nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate liquid stream, the method further includes passing the purified filtrate liquid stream through a solvent extraction reactor and mixing with an extractant and an organic phase to further remove impurities (*e.g.*, copper (Cu), iron (Fe), and optionally aluminum (Al)) from the intermediate liquid stream.

[0050] In one further example, a total cumulative concentration of impurities comprising a metal selected from the group consisting of: copper (Cu), iron (Fe), aluminum (Al), and combinations thereof is less than or equal to about 20 ppm.

[0051] In one further example, the extractant comprises bis-(2-ethylhexyl) phosphoric acid and the organic phase comprises kerosene.

[0052] In one example, the introducing the intermediate liquid stream into a lithium precipitation reactor comprises adding sodium carbonate (Na_2CO_3) and a second inorganic

base to the lithium precipitation reactor. The intermediate liquid stream has a temperature of greater than or equal to about 80°C to less than or equal to about 90°C for greater than or equal to about 90 minutes to generate lithium carbonate (Li_2CO_3) precipitate.

[0053] In one example, the intermediate liquid stream comprises lithium sulfate (Li_2SO_4) and sodium sulfate (Na_2SO_4). Prior to the introducing, the intermediate liquid stream is subjected to a thermal shock process so that a temperature is greater than or equal to about 0°C to less than or equal to about 30°C followed by ionization in an electrode ionization unit to facilitate precipitation of sodium sulfate (Na_2SO_4) from the intermediate liquid stream, followed by adding sodium carbonate (Na_2CO_3) into the lithium precipitation reactor to generate lithium carbonate (Li_2CO_3) precipitate.

[0054] In one example, a separation efficiency for each of copper (Cu), aluminum (Al), titanium (Ti), and iron (Fe) is respectively greater than or equal to about 95% and a separation efficiency for fluorine is greater than or equal to about 80%.

[0055] In a further example, a separation efficiency for each of copper (Cu), aluminum (Al), titanium (Ti), and iron (Fe) is respectively greater than or equal to about 99.5% and a separation efficiency for fluorine is greater than or equal to about 99%.

[0056] According to another example of the present disclosure, a process for recovering metals from a lithium-ion battery waste stream is provided. The process may comprise purifying a lithium-ion battery waste liquid stream comprising sulfuric acid (H_2SO_2) in a first reactor to remove fluorine (F), phosphate (P), and one or more impurity metals selected from the group consisting of: copper (Cu), aluminum (Al), iron (Fe), and titanium (Ti). The purifying may include adding a source of iron (Fe) and a first inorganic base to the waste liquid stream to precipitate copper (Cu) via a cementation reaction,

followed by adding a source of calcium oxide and an oxidant to generate calcium fluoride (CaF_2) that precipitates out of the waste liquid stream. The purifying may also include adding a second inorganic base to increase pH of the waste liquid stream to generate one or more metal precipitate compounds selected from the group consisting of: aluminum hydroxide ($Al(OH)_3$), titanium hydroxide ($Ti(OH)_4$), iron phosphate ($FePO_4$), and one or more iron hydroxides ($Fe(OH)_3$ and $Fe(OH)_2$). The process also comprises passing the waste liquid stream exiting the first reactor through a filter to generate a purified filtrate liquid stream and a second retentate comprising the one or more metal precipitate compounds, copper (Cu), and calcium fluoride (CaF_2). Next, the process includes separating nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate liquid stream by passing the purified filtrate liquid stream into either a second reactor for conducting a co-precipitation process by increasing pH or one or more chromatographic columns or packed-bed columns/reactors. In this manner, an intermediate liquid stream comprising lithium (Li) and one or more recovered products comprising one or more of nickel (Ni), manganese (Mn), and cobalt (Co) is generated. The one or more recovered products are removed from the intermediate liquid stream. The process also comprises introducing the intermediate liquid stream into a lithium precipitation reactor to precipitate at least one compound comprising lithium (Li).

[0057] In one example, the source of iron (Fe) comprises iron powder, the first inorganic base and the second inorganic base each comprise sodium hydroxide (NaOH), the source of calcium oxide is selected from the group consisting of: lime (CaO), calcium hydroxide ($Ca(OH)_2$), and combinations thereof, and the oxidant is selected from the group

consisting of: hydrogen peroxide (H_2O_2), ozone (O_3), sodium hypochlorite (NaClO), and combinations thereof.

[0058] In one example, the first base is added until pH is about 5, the second base is added until pH is about 10.5, and the oxidant comprises hydrogen peroxide (H_2O_2) which is added at a concentration of greater than or equal to about 4 % by volume to less than or equal to about 6% by volume of total liquid contents (waste liquid stream).

[0059] In one example, the adding the source of iron (Fe) and the first inorganic base to the waste liquid stream is conducted at a pH of greater than or equal to about 1 to less than or equal to about 2 while mixing for a duration of greater than or equal to about 15 minutes at a temperature of greater than or equal to about 55°C to less than or equal to about 65°C.

[0060] In one example, about 2.5 g of iron powder is added for each liter (L) of the waste liquid stream.

[0061] In one example, the adding the source of calcium oxide and the oxidant to generate calcium fluoride (CaF_2) is conducted at a pH of greater than or equal to about 1 to less than or equal to about 2 while mixing for a duration of greater than or equal to about 30 minutes at a temperature of greater than or equal to about 55°C to less than or equal to about 65°C.

[0062] In one example, the adding of the second inorganic base increases the pH of the waste liquid stream to greater than or equal to about 4 to less than or equal to about 5.

[0063] In one example, the adding of the second inorganic base to increase pH is conducted while mixing for a duration of greater than or equal to about 60 minutes at a temperature of greater than or equal to about 55°C to less than or equal to about 65°C.

[0064] In one example, the purified filtrate liquid stream comprises nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) and the separating nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate liquid stream occurs by passing the purified filtrate liquid stream into the second reactor. In the second reactor, the co-precipitation process is conducted that comprises increasing the pH of the purified filtrate liquid stream to greater than or equal to about 11 in an inert environment to form nickel hydroxide hydrate ($Ni(OH)_2 \cdot 6H_2O$), manganese hydroxide hydrate ($Mn(OH)_2 \cdot H_2O$), and cobalt hydroxide hydrate ($Co(OH)_2 \cdot 7H_2O$) that concurrently precipitate from the purified filtrate liquid stream to generate the one or more recovered products.

[0065] In one further example, the increasing the pH of the purified filtrate liquid stream further comprises first adding ammonia to the purified liquid stream that comprises nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$).

[0066] In one example, the one or more recovered products is an electroactive material precursor having a stoichiometry of $Ni_xMn_yCo_{1-x-y}(OH)_2$, where x is < 1 and y is < 1.

[0067] In one example, the one or more recovered products has a stoichiometry of about $\frac{1}{3}Ni(OH)_2 + \frac{1}{3}Mn(OH)_2 + \frac{1}{3}Co(OH)_2 \rightarrow Ni_{0.33}Mn_{0.33}Co_{0.33}(OH)_2$.

[0068] In one example, the process further comprises determining a first ratio of Ni:Mn:Co in the purified filtrate liquid stream prior to the co-precipitation process. The first ratio is then compared to a target stoichiometric ratio of Ni:Mn:Co for the one or more recovered products. Thus, the process may include adding one or more of nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) to the purified filtrate liquid stream to adjust an amount of nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$),

and cobalt sulfate ($CoSO_4$) prior to adjusting the pH. In this manner, the one or more recovered products has a second ratio corresponding to the target stoichiometric ratio.

[0069] In one example, the separating occurs by passing the purified filtrate liquid stream in a first direction in a packed-bed column/reactor comprising a chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 4.5 that generates a raffinate stream comprising at least one manganese (Mn)-containing species and at least one lithium (Li)-containing species that exits the packed-bed column/reactor, while nickel (Ni) ions and cobalt (Co) ions are retained on the chelating resin in the packed-bed column/reactor. The process further includes regenerating the packed-bed column/reactor by passing a regeneration liquid having a pH of less than or equal to about 1.5 in the packed-bed column/reactor to form an extract stream comprising the nickel (Ni) ions and cobalt (Co) ions. The process also includes precipitating nickel hydroxide ($Ni(OH)_2$) and cobalt hydroxide ($Co(OH)_2$) from the extract.

[0070] In one example, the method further comprises forming a precursor of $LiNiCoAlO_2$ electroactive material by combining the nickel hydroxide ($Ni(OH)_2$) and cobalt hydroxide ($Co(OH)_2$) with the aluminum hydroxide ($Al(OH)_3$) and at least one compound comprising lithium (Li).

[0071] In one example, the process further comprises adjusting the pH of the purified filtrate liquid stream to be greater than or equal to about 4 to less than or equal to about 5 as it enters the packed-bed column/reactor. The process further comprises precipitating manganese hydroxide ($Mn(OH)_2$) by adjusting pH to be greater than or equal to about 8 to less than or equal to about 10 and separating the manganese hydroxide ($Mn(OH)_2$).

[0072] In one example, the at least one compound comprising lithium (Li) comprises lithium carbonate (Li_2CO_3) that is combined with manganese hydroxide ($Mn(OH)_2$) to form $LiMnO_4$ electroactive material.

[0073] In one example, the adjusting the pH comprises adding sodium hydroxide (NaOH) to the purified filtrate liquid stream.

[0074] In one example, a stationary phase in the packed-bed column/reactor comprises a macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid.

[0075] In one example, the separating occurs by passing the purified filtrate liquid stream in a first direction in a first packed-bed column/reactor comprising a first chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 1.5. This generates a first raffinate stream comprising at least one manganese (Mn)-containing species, at least one cobalt (Co)-containing species, and at least one lithium (Li)-containing species that exits the first packed-bed column/reactor, while nickel (Ni) ions are retained on the first chelating resin in the first packed-bed column/reactor. The process also comprises passing the first raffinate stream in a first direction in a second packed-bed column/reactor comprising a second chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 2.5 that generates a second raffinate stream comprising at least one manganese (Mn)-containing species and at least one lithium (Li)-containing species that exits the second packed-bed column/reactor, while cobalt (Co) ions are retained on the second chelating resin in the second packed-bed column/reactor. The process further comprises regenerating the first packed-bed column/reactor by passing a first regeneration liquid having a pH of less than

or equal to about 1.5 in the first packed-bed column/reactor to form a first extract stream comprising the nickel (Ni) ions. Next, nickel hydroxide ($Ni(OH)_2$) may be precipitated from the first extract stream. The process also includes regenerating the second packed-bed column/reactor by passing a second regeneration liquid having a pH of less than or equal to about 2.5 in the second packed-bed column/reactor to form a second extract stream comprising the cobalt (Co) ions. This is followed by precipitating cobalt hydroxide ($Co(OH)_2$) from the second extract stream.

[0076] In one example, the process further comprises forming a precursor of $LiNiCoAlO_2$ electroactive material by combining the nickel hydroxide ($Ni(OH)_2$) and cobalt hydroxide ($Co(OH)_2$) with the aluminum hydroxide ($Al(OH)_3$) and the at least one compound comprising lithium (Li).

[0077] In one example, the process further comprises precipitating manganese hydroxide ($Mn(OH)_2$) from the second raffinate stream by adjusting pH to be greater than or equal to about 8 to less than or equal to about 10 thus forming the intermediate liquid stream. The manganese hydroxide ($Mn(OH)_2$) is then separated from the intermediate liquid stream.

[0078] In one example, the at least one compound comprising lithium (Li) comprises lithium carbonate (Li_2CO_3) that is combined with manganese hydroxide ($Mn(OH)_2$) to form $LiMnO_4$ electroactive material.

[0079] In one example, the process further comprises adjusting the pH of the purified filtrate liquid stream by adding sodium hydroxide (NaOH) to the purified filtrate liquid stream to have a pH of about 2.5 and adjusting the pH of the first raffinate stream by adding sodium hydroxide (NaOH) to the first raffinate stream to have a pH of about 3.5.

[0080] In one example, a stationary phase in the first packed-bed column/reactor comprises macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid and a stationary phase in the second packed-bed column/reactor comprises macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid.

[0081] In one example, the lithium-ion battery waste stream is black mass. Prior to the purifying, the method further comprises generating the lithium-ion battery waste liquid stream by subjecting the black mass to a leaching process that comprises mixing an inorganic acid with the black mass to form an acidic admixture. An oxidant may be mixed with the acidic admixture. The process may further include adding deionized water to the acidic admixture. Then, a leachate stream is passed through a second filter to generate a filtrate liquid stream comprising one or more metal sulfates and a first retentate comprising graphite.

[0082] In one further example, both the mixing of the inorganic acid and the mixing of the oxidant are conducted at a temperature of less than or equal to about 100°C.

[0083] In one further example, the inorganic acid comprises sulfuric acid (H_2SO_4), the oxidant comprises hydrogen peroxide (H_2O_2), and a pH of the acidic admixture is less than or equal to about 2.5.

[0084] In one further example, the mixing the inorganic acid comprises adding black mass to the sulfuric acid (H_2SO_4) having a molarity of about 4M, the mixing the oxidant comprises adding about 30% by mass hydrogen peroxide (H_2O_2) to the acidic admixture so that the acidic admixture has a solid/liquid ratio of 100 g/L, followed by mixing for greater than or equal to about 2 hours, and then the adding of the deionized water dilutes the

sulfuric acid (H_2SO_4) to a molarity of about 2M, followed by mixing for greater than or equal to about 30 minutes.

[0085] In one example, the one or more recovered products has a purity level of greater than or equal to about 95% and comprises less than or equal to about 5% by mass of a total cumulative amount of impurities comprising aluminum (Al), copper (Cu), iron (Fe), phosphorus (P), titanium (Ti) and fluorine (F).

[0086] In one example, the one or more recovered products has a purity level of greater than or equal to about 98% and comprises less than or equal to about 2% by mass of a total cumulative amount of impurities comprising aluminum (Al), copper (Cu), iron (Fe), phosphorus (P), titanium (Ti) and fluorine (F).

[0087] In one example, the separating recovers greater than or equal to about 80% by mass of each of nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate liquid stream.

[0088] In one example, the introducing the intermediate liquid stream into a lithium precipitation reactor comprises adding sodium carbonate (Na_2CO_3) and a second inorganic base to the lithium precipitation reactor. The intermediate liquid stream has a temperature of greater than or equal to about 80°C to less than or equal to about 90°C for greater than or equal to about 90 minutes to generate lithium carbonate (Li_2CO_3) precipitate.

[0089] In one example, the intermediate liquid stream comprises lithium sulfate (Li_2SO_4) and sodium sulfate (Na_2SO_4). Prior to the introducing, the intermediate liquid stream is subjected to a thermal shock process so that a temperature is greater than or equal to about 0°C to less than or equal to about 30°C followed by ionization in an electrode ionization unit to facilitate precipitation of sodium sulfate (Na_2SO_4) from the intermediate

liquid stream, followed by adding sodium carbonate (Na_2CO_3) into the lithium precipitation reactor to generate lithium carbonate (Li_2CO_3) precipitate.

[0090] In one example, a separation efficiency for each of copper (Cu), aluminum (Al), titanium (Ti), and iron (Fe) is respectively greater than or equal to about 95% and a separation efficiency for fluorine is greater than or equal to about 80%.

[0091] In a further example, a separation efficiency for each of copper (Cu), aluminum (Al), titanium (Ti), and iron (Fe) is respectively greater than or equal to about 99.5% and a separation efficiency for fluorine is greater than or equal to about 99%.

[0092] According to yet another example of the present disclosure, a system for recovering metals from a lithium-ion battery waste stream is provided. The system may comprise a leaching reactor unit comprising a first heated reactor tank having an agitator, a source of sulfuric acid (H_2SO_4), a source of hydrogen peroxide (H_2O_2), and a source of deionized water (H_2O), and a first filter downstream of the first heated reactor tank. The first heated reactor tank has a plurality of inlets that receive the lithium-ion battery waste liquid stream comprising black mass, sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), and deionized water (H_2O) and an outlet through which a leachate stream exits to enter the first filter for separation into a first filtrate liquid stream and a first retentate comprising graphite. The system also comprises an impurity reactor removal unit comprising a second heated reactor tank having an agitator, a source of hydrogen peroxide (H_2O_2), a source of calcium oxide, and a second filter downstream of the second heated reactor tank. The second heated reactor tank has a plurality of inlets that receive the first filtrate liquid stream, iron (Fe) powder, sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), calcium oxide, and an outlet through which a first intermediate liquid exits the second reactor tank to enter

the second filter for separation into a purified filtrate liquid stream and a second retentate comprising a plurality of precipitated compounds comprising fluorine (F), phosphate (P), copper (Cu), aluminum (Al), iron (Fe), and titanium (Ti). The system also comprises a metal recovery unit for separating nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate liquid stream by in a separation unit. The separation unit may comprise one or more of: a co-precipitation unit and/or one or more chromatographic columns or packed-bed columns/reactors. Where the separation unit is a co-precipitation unit, it comprises a third heated reactor tank for conducting a co-precipitation process by increasing pH, a source of nickel sulfate ($NiSO_4$), a source of manganese sulfate ($MnSO_4$), a source of cobalt sulfate ($CoSO_4$), a source of sodium hydroxide (NaOH), the third heated reactor tank having an agitator and a plurality of inlets that receive the purified filtrate liquid stream, a source of nickel sulfate ($NiSO_4$), a source of manganese sulfate ($MnSO_4$), a source of cobalt sulfate ($CoSO_4$), a source of sodium hydroxide (NaOH), and an outlet through which a second intermediate liquid exits the third heated reactor tank and enters a third filter downstream of the separation unit for separation. Alternatively, the separation unit may be one or more chromatographic columns or packed-bed columns/reactors that generate the second intermediate liquid stream that enters a third filter downstream of the one or more chromatographic columns or packed-bed columns/reactors. There is also a third filter downstream of the separation unit through which the second intermediate liquid stream passes for separation into a third intermediate liquid stream and a third retentate comprising one or more recovered products comprising nickel (Ni), manganese (Mn), and cobalt (Co). Finally, the system comprises a lithium recovery unit that includes a lithium precipitation reactor to precipitate at least one compound comprising lithium (Li) and a fourth filter

downstream of the fourth heated reactor tank. The lithium precipitation reactor has an outlet through which a fourth intermediate stream exits to enter a fourth filter for separation into a waste stream and a fourth retentate comprising the at least one compound comprising lithium (Li). In one example, the impurity reactor removal unit further comprises a source of iron (Fe) powder and a source of sodium hydroxide (NaOH) and wherein the plurality of inlets of the second heated reactor tank further receives the iron (Fe) powder and sodium hydroxide (NaOH).

[0093] In one example, the impurity reactor removal unit further comprises a source of sodium phosphate (Na_3PO_4).

[0094] In one example, the lithium precipitation reactor is a fourth heated reactor tank having an agitator and the lithium recovery unit further comprises a source of sodium hydroxide (NaOH), a source of sodium carbonate (Na_2CO_3). The fourth heated reactor tank has a plurality of inlets that receive the third intermediate liquid stream, sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3), and an outlet through which the fourth intermediate stream exits to enter the fourth filter.

[0095] In one example, the lithium recovery unit further comprises a thermal shock unit and an electrode ionization unit upstream of the lithium precipitation reactor.

[0096] In one example, the metal recovery unit is the co-precipitation unit that further comprises an analyzer to determine a content of nickel (Ni), manganese (Mn), and cobalt (Co) in the purified filtrate liquid stream upstream of the third heated reactor. The co-precipitation unit also comprises a controller and one or more metering pumps to regulate flow of a nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$)

into the plurality of inlets of the third heated reactor. The controller receives input from the analyzer and controls the one or more metering pumps.

[0097] In one example, the metal recovery unit comprises one chromatographic column or packed-bed column/reactor comprising a chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 4.5. The metal recovery unit also comprises one or more precipitation reactors for precipitating compounds comprising nickel (Ni), manganese (Mn), and cobalt (Co).

[0098] In one example, a stationary phase in the packed-bed column/reactor comprises a macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid.

[0099] In one example, the metal recovery unit comprises a first chromatographic column or packed-bed column/reactor comprising a first chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 2.5, a second chromatographic column or packed-bed column/reactor comprising a second chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 3.5, and one or more precipitation reactors for precipitating compounds comprising nickel (Ni), manganese (Mn), and cobalt (Co).

[0100] In one example, the system further comprises an evaporator downstream of the metal recovery unit and upstream of the lithium recovery unit.

[0101] According to another example of the present disclosure, a system for recovering metals from a lithium-ion battery waste stream is provided. The system may comprise a leaching reactor unit comprising a first heated reactor tank having an agitator, a source of sulfuric acid (H_2SO_4), a source of hydrogen peroxide (H_2O_2), and a source of

deionized water (H_2O), and a first filter downstream of the first heated reactor tank. The first heated reactor tank has a plurality of inlets that receive the lithium-ion battery waste liquid stream comprising black mass, sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), and deionized water (H_2O) and an outlet through which a leachate stream exits to enter the first filter for separation into a first filtrate liquid stream and a first retentate comprising graphite. The system also comprises an impurity reactor removal unit comprising a second heated reactor tank having an agitator, a source of iron (Fe) powder, a source of sodium hydroxide (NaOH), a source of hydrogen peroxide (H_2O_2), a source of calcium oxide, and a second filter downstream of the second heated reactor tank. The second heated reactor tank has a plurality of inlets that receive the first filtrate liquid stream, iron (Fe) powder, sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), calcium oxide (*e.g.*, CaO, $Ca(OH)_2$), and an outlet through which a first intermediate liquid exits the second reactor tank to enter the second filter for separation into a purified filtrate liquid stream and a second retentate comprising a plurality of precipitated compounds comprising fluorine (F), phosphate (P), copper (Cu), aluminum (Al), iron (Fe), and titanium (Ti). The system also comprises a metal recovery unit for separating nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate liquid stream by in a separation unit. The separation unit may comprise either a co-precipitation unit or one or more chromatographic columns or packed-bed columns/reactors. Where the separation unit is a co-precipitation unit, it comprises a third heated reactor tank for conducting a co-precipitation process by increasing pH, a source of nickel sulfate ($NiSO_4$), a source of manganese sulfate ($MnSO_4$), a source of cobalt sulfate ($CoSO_4$), a source of sodium hydroxide (NaOH), the third heated reactor tank having an agitator and a plurality of inlets that receive the purified filtrate

liquid stream, a source of nickel sulfate ($NiSO_4$), a source of manganese sulfate ($MnSO_4$), a source of cobalt sulfate ($CoSO_4$), a source of sodium hydroxide (NaOH), and an outlet through which a second intermediate liquid exits the third heated reactor tank and enters a third filter downstream of the separation unit for separation. Alternatively, the separation unit may be one or more chromatographic columns or packed-bed column/reactor that generate the second intermediate liquid stream that enters a third filter downstream of the one or more chromatographic columns or packed-bed columns/reactors. There is also a third filter downstream of the separation unit through which the second intermediate liquid stream passes for separation into a third intermediate liquid stream and a third retentate comprising one or more recovered products comprising nickel (Ni), manganese (Mn), and cobalt (Co). Finally, the system comprises a lithium recovery unit that includes a lithium precipitation reactor to precipitate at least one compound comprising lithium (Li) and a fourth filter downstream of the fourth heated reactor tank. The lithium precipitation reactor has an outlet through which a fourth intermediate stream exits to enter a fourth filter for separation into a waste stream and a fourth retentate comprising the at least one compound comprising lithium (Li).

[0102] In one example, the lithium precipitation reactor is a fourth heated reactor tank having an agitator and the lithium recovery unit further comprises a source of sodium hydroxide (NaOH), a source of sodium carbonate (Na_2CO_3). The fourth heated reactor tank has a plurality of inlets that receive the third intermediate liquid stream, sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3), and an outlet through which the fourth intermediate stream exits to enter the fourth filter.

[0103] In one example, the lithium recovery unit further comprises a thermal shock unit and an electrode ionization unit upstream of the lithium precipitation reactor.

[0104] In one example, the metal recovery unit is the co-precipitation unit that further comprises an analyzer to determine a content of nickel (Ni), manganese (Mn), and cobalt (Co) in the purified filtrate liquid stream upstream of the third heated reactor. The co-precipitation unit also comprises a controller and one or more metering pumps to regulate flow of a nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) into the plurality of inlets of the third heated reactor. The controller receives input from the analyzer and controls the one or more metering pumps.

[0105] In one example, the metal recovery unit comprises one chromatographic column or packed-bed column/reactor comprising a chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 4.5. The metal recovery unit also comprises one or more precipitation reactors for precipitating compounds comprising nickel (Ni), manganese (Mn), and cobalt (Co).

[0106] In one example, a stationary phase in the packed-bed column/reactor comprises a macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid.

[0107] In one example, the metal recovery unit comprises a first chromatographic column or packed-bed column/reactor comprising a first chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 2.5, a second chromatographic column or packed-bed column/reactor comprising a second chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about

3.5, and one or more precipitation reactors for precipitating compounds comprising nickel (Ni), manganese (Mn), and cobalt (Co).

[0108] In one example, the system further comprises an evaporator downstream of the metal recovery unit and upstream of the lithium recovery unit.

[0109] According to yet another example of the present disclosure, a system for recovering metals from a lithium-ion battery waste stream is provided. The system comprises a leaching reactor. The leaching reactor comprises a plurality of inlets that receive the lithium-ion battery waste liquid stream comprising black mass, sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), and deionized water (H_2O). The leaching reactor also has at least one outlet and an agitator. Further, the leaching reactor is in thermal communication with a first heat source and is configured to subject the lithium-ion battery waste stream to a leaching reaction that generates a leachate stream. The system also includes a first pneumatic filter in fluid communication with the outlet of the leaching reactor and through which the leachate stream passes and is separated into a first filtrate liquid stream and a first retentate comprising graphite. The system also comprises an impurity removal reactor in fluid communication with the first pneumatic filter. The impurity removal reactor comprises a plurality of inlets that receive the first filtrate liquid stream from the first pneumatic filter, hydrogen peroxide (H_2O_2), and calcium oxide (*e.g.*, CaO, $Ca(OH)_2$). The impurity removal reactor also comprises an outlet and an agitator. The impurity removal reactor is in thermal communication with a second heat source and is configured to purify the first filtrate liquid stream to remove fluorine (F), phosphate (P), and one or more impurity metals selected from the group consisting of: copper (Cu), aluminum (Al), iron (Fe), and titanium (Ti) and generate a first intermediate liquid stream.

precipitation reactor is in thermal communication with a fourth heat source and is configured to generate a product stream. A fourth pneumatic filter is in fluid communication with the outlet of the lithium precipitation reactor and the product stream passes through it, so that it is separated into a fourth retentate comprising lithium carbonate (Li_2CO_3) product and a waste stream. The system also comprises a fluid conduit for establishing fluid communication between the leaching reactor, the first pneumatic filter, the impurity removal reactor, the second pneumatic filter, the co-precipitation reactor, the third pneumatic filter, the evaporator, the lithium precipitation reactor, and the fourth pneumatic filter. The system also has at least one pump for circulating fluids within the fluid conduit.

[0110] In one example, the plurality of inlets of the impurity removal reactor further receives iron (Fe) powder and sodium hydroxide (NaOH).

[0111] In one example, the plurality of inlets of the impurity removal reactor further receives sodium phosphate (Na_3PO_4).

[0112] In one example, the leaching reactor comprises a first outlet through which the leachate stream flows and a second outlet through which a first gas effluent flows. The co-precipitation reactor comprises a third outlet through which the second intermediate liquid stream flows and a fourth outlet through which a second gas effluent flows. The system further comprises a scrubber in fluid communication with the second outlet of the leaching reactor and the fourth outlet of the co-precipitation reactor so that the scrubber receives the first gas effluent and second gas effluent for processing.

[0113] According to yet another example of the present disclosure, a system for recovering metals from a lithium-ion battery waste stream is provided. The system

leaching reactor, the first pneumatic filter, the impurity removal reactor, the second pneumatic filter, the co-precipitation reactor, the third pneumatic filter, the evaporator, the lithium precipitation reactor, and the fourth pneumatic filter. The system also has at least one pump for circulating fluids within the fluid conduit.

[0114] In one example, the leaching reactor comprises a first outlet through which the leachate stream flows and a second outlet through which a first gas effluent flows. The co-precipitation reactor comprises a third outlet through which the second intermediate liquid stream flows and a fourth outlet through which a second gas effluent flows. The system further comprises a scrubber in fluid communication with the second outlet of the leaching reactor and the fourth outlet of the co-precipitation reactor so that the scrubber receives the first gas effluent and second gas effluent for processing.

[0115] Further aspects and areas of applicability will become apparent from the description provided herein. It should be understood that various aspects of this disclosure may be implemented individually or in combination with one or more other aspects. It should also be understood that the description and specific examples herein are intended for purposes of illustration only and are not intended to limit the scope of the present disclosure.

DRAWINGS

[0116] The drawings described herein are for illustrative purposes only of selected embodiments and not all possible implementations, and are not intended to limit the scope of the present disclosure.

[0163] In certain aspects, the present disclosure contemplates a process for recovering metals from a lithium-ion battery waste stream. An optional first leaching step may be conducted on a lithium-ion battery waste stream, for example, comprising a black mass (2) that is subjected to a leaching process, or the waste stream may be received pre-processed, as will be described further below. For example, a process of removing impurities and recovering various precious metals from one or more spent lithium-ion batteries according to one example embodiment of the present disclosure is illustrated in Fig. 1 and indicated generally by the reference number 100. As shown, a process may be conducted in system 100 that includes various consecutively arranged stages including a leaching unit or stage 102, an impurity removal unit or stage 104, and two precipitation units or stages 106, 108. In the stages 102, 104, 106, 108, contents are collected and processed in reactors or vessels 110, 122, 132, 142. Each reactor 110, 122, 132, 142 may be a jacketed, agitated tank that is internally coated with a corrosion-resistant lining to withstand hot acidic conditions that may occur in the system 100. For example, each reactor 110, 122, 132, 142 may include an agitator 112, 124, 134, 148 for stirring contents, and a jacket 116, 126, 136, 150 surrounding its respective reactor to circulate a heating/cooling medium (*e.g.*, steam, etc.) for maintaining a desired temperature.

[0164] The process in the system 100 begins at the leaching stage 102. In the example of Fig. 1, various components are fed into the reactor (*e.g.*, a leaching reactor) 110, which is identified as V-001. The method may include generating the lithium-ion battery waste liquid stream by subjecting the black mass (2) to a leaching process that comprises mixing an inorganic acid (1) with the black mass (2) to form an acidic admixture; then mixing an oxidant (3) with the acidic admixture; and adding deionized water (4) to the acidic

admixture. After this process, the leachate stream (5) generated in the reactor 110 may then pass through a second filter to generate a filtrate liquid stream (7) comprising one or more metal sulfates and a first retentate comprising graphite (6).

[0165] Thus, during the leaching stage 102, an inorganic acid from a source or container (1) is fed into the leaching reactor 110 during a first phase. The inorganic acid may be sulfuric acid (H_2SO_4) as shown in Fig. 1 or another suitable inorganic acid. Notably, in certain aspects, hydrochloric acid (HCl) may be avoided, because chlorine can cause contamination in electrochemical cells if the recycled material contains high levels of chlorine. In some examples, the inorganic acid may contain about 4M sulfuric acid (H_2SO_4). During this time, the agitator 112 may be activated to stir the acid solution in the leaching reactor 110. In one aspect, the mixing of the inorganic acid and the mixing of the oxidant are conducted at a temperature of less than or equal to about 100°C, optionally less than or equal to about 95°C, and in certain aspects, less than or equal to about 90°C. The oxidant may be hydrogen peroxide (H_2O_2), ozone (O_3), sodium hypochlorite (NaClO), or combinations thereof. In certain variations, the oxidant is hydrogen peroxide (H_2O_2). Notably, because the addition of black mass and dilution with sulfuric acid are exothermic processes, the temperature may be monitored to ensure that it does not exceed the boiling point of water, for example, by introducing cool water or via heat exchangers. During the first phase, black mass from a source or container may be gradually added to the agitated acid solution in the leaching reactor 110.

[0166] In one variation, the inorganic acid comprises sulfuric acid (H_2SO_4), the oxidant comprises hydrogen peroxide (H_2O_2), and a pH of the acidic admixture in the leaching reactor 110 is less than or equal to about 2.5. The hydrogen peroxide (H_2O_2) may

be added at a concentration of greater than or equal to about 4 % by volume to less than or equal to about 6% by volume of total liquid contents. In one further variation, the mixing of the inorganic acid comprises adding black mass to the sulfuric acid (H_2SO_4) having a molarity of about 4M, the mixing the oxidant adds about 30% by mass hydrogen peroxide (H_2O_2) to the acidic admixture so that the acidic mixture has a solid/liquid ratio of 100 g/L, followed by mixing in the leaching reactor 110 for greater than or equal to about 2 hours, and then the adding of the deionized water dilutes the sulfuric acid (H_2SO_4) to a molarity of about 2M, followed by mixing for greater than or equal to about 30 minutes.

[0167] After the black mass (2) is introduced, the acid solution begins reacting with metals in the black mass so that the metals react and form their respective sulfates. In some examples, fluorine (F) in the black mass may be converted to hydrogen fluoride (HF). Some of the HF may stay in the solution contained in the leaching reactor 110, while the remainder may be released as a gas (80) and vented to a scrubber 114.

[0168] During the first phase, an oxidant may be fed to the leaching reactor 110 from a source or container. The oxidant may be hydrogen peroxide (H_2O_2) as shown in Fig. 1 or another suitable oxidant. In some examples, the oxidant may be 30% hydrogen peroxide (H_2O_2). The oxidant may be fed into the reactor 110 before, the same time as, or after the inorganic acid and/or the black mass are added. The mixture of the acid solution, the oxidant, and the black mass may be agitated for a defined period of time (*e.g.*, 1 hour, 2 hours, 3 hours, etc.).

[0169] In some examples, it may be desired for a temperature of the liquid in the leaching reactor 110 to remain at a defined level, as noted above, desirably below 100°C. For example, the defined temperature level may range from about 60 °C (140 °F) to about

80 °C (176 °F). In some embodiments, the minimum required temperature level may be about 60 °C (140 °F), and a desired temperature level may be about 80 °C (176 °F). In some cases, however, the temperature of the liquid may increase above the desired level and/or fall below the minimum required temperature level. For example, as noted above, heat from the reaction between the acid solution and the metals in the black mass may increase the temperature of the liquid in the leaching reactor 110 above the desired temperature (*e.g.*, 80 °C). In other examples, the liquid temperature may not rise to the required level (*e.g.*, 60 °C). In such examples, the liquid temperature may be controlled through different manners. For example, the liquid temperature may be reduced by adjusting the rate of black mass addition to the acid solution. In other cases, the liquid temperature may be reduced or increased by circulating a heating/cooling medium (*e.g.*, steam, etc.) through the jacket 116 surrounding the leaching reactor 110.

[0170] Once the agitation period is complete, demineralized water from a source or container (4) is added to the reactor 110 in a second phase. For example, deionized (DI) water may be added to dilute the sulfuric acid. For instance, adding the water may reduce molarity of the liquid in the leaching reactor 110 from about 4M to about 2M. Additionally, the water may cool the contents in the reactor 110 so that the temperature does not exceed 90 – 100 °C, because as noted above, the addition of the black mass and dilution of the sulfuric acid are exothermic processes. In some examples, the temperature may be cooled to about 60 °C (140 °F). After the demineralized water is added, the mixture in the leaching reactor 110 is agitated for a defined period of time (*e.g.*, about 30 minutes, etc.). At this point, the pH of the solution may be acidic, for example, greater than or equal to about 0.1 to less than or equal to about 1. In certain variation, the pH may be about 0.1. The leachate

stream may comprise a variety of metal sulfates, for example, nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), cobalt sulfate ($CoSO_4$), and the like.

[0171] Next, the vessel contents in the reactor 110 are pumped via a pump 118 through a filter 120, which may be a pneumatic filter. After passing the leachate stream through the filter, a filtrate liquid stream (7) comprising one or more metal sulfates and a first retentate comprising solids (6), such as carbon (graphite) particles are formed. In this manner, the graphite is removed from the leachate stream. The pump 118 and the filter 120 are identified as P-001 and F-001, respectively, in Fig. 1. The remaining contents (*e.g.*, a first filtrate) passing through the filter 120 are fed to an impurity removal reactor 122 used in the impurity removal stage 104. In some examples, nearly all carbon (graphite) particles in the vessel contents may be captured in the filter 120 as retentate. Such carbon (graphite) particles may be passed or conveyed to a container and further processed (*e.g.*, dried). In some examples, the pump 118 may be a centrifugal pump as shown in Fig. 1 or another suitable pump, and the filter 120 may be a pressure filter, a hydraulic filter, a gravity filter or another suitable type of filter.

[0172] After filtration, the reactor 110 may be washed with an internal spray ball to remove acid residue and to send all leaching reaction products to the reactor 122.

[0173] Additionally, acid residue in the filter cake/retentate may be neutralized by rinsing the residue to reduce operator exposure during cake collection. In some examples, a separate water stream may be lined up with the pump 118 and a dilute caustic may be added upstream of the filter 120 to remove residual filtrate, which may be sent to wastewater treatment. At the end this stage 102, graphite cake (*e.g.*, in the container, on the filter 120, etc.) may be collected for disposal.

[0174] In the impurity removal stage 104, impurities removal occurs. This may occur concurrently and multifacetedly in a collective batch process, and with individual steps to remove specific impurities performed sequentially. If the impurities removal procedure is not followed chronologically or sequentially as explained below, high efficiency for impurities removal may not be achieved. In the impurity removal stage 104, impurities (*e.g.*, certain metals) in the leachate (7) produced from stage 102 may be removed, for example, converted to their hydroxide or other forms and precipitated. In some embodiments, there may be a minimal compromission of precious metals concentration of not more than 2% while removing impurities.

[0175] In certain aspects, the methods of the present disclosure may include purifying the lithium-ion battery waste liquid stream (7) comprising sulfuric acid (H_2SO_4) in an impurity removal reactor 122 to remove fluorine (F), phosphate (P), and one or more impurity metals selected from the group consisting of: copper (Cu), aluminum (Al), iron (Fe), and titanium (Ti). Initially, the contents (*e.g.*, the first filtrate or leachate) (7) from the reactor 110 are provided to the impurity removal reactor 122, which is identified as V-002 in FIG. 1. The purifying may include removing copper (Cu) from the liquid stream. In certain variations, the purifying may include precipitating a product comprising copper (Cu) that is removed (*e.g.*, separated) from the liquid stream, which may occur via a cementation reaction or sulfidation reaction, for example. In other aspects, the removing of copper (Cu) may include subjecting the the removing copper (Cu) from the waste liquid stream comprises subjecting the waste liquid stream to a solvent-extraction. The removing of the copper (Cu) may involve one or more of these removal processes (*e.g.*, one or more of sulfidation, cementation, or solvent-extraction).

[0180] Another sulfidation reaction that may occur when sodium sulfide is added is:

$$Na_2S(s) + Cu^{2+}(aq) \rightarrow CuS(s) + 2Na^{+}(aq).$$

Thus, in one aspect, the overall sulfidation reaction in the waste liquid may be represented by:

$$Na_2S(aq) + CuSO_4(aq) \rightarrow Na_2SO_4 + CuS(s).$$

[0181] In certain variations, a pH during the sulfidation reaction may be greater than or equal to about 0.7 to less than or equal to about 2, in one variation, optionally greater than or equal to about 1.5 to less than or equal to about 2. The sulfidation reaction may be conducted at about 25°C. The sulfidation reaction may be conducted for about 30 minutes in certain variations.

[0182] The copper precipitate formed via the sulfidation reaction may then be removed from the liquid stream. The precipitated copper (Cu) can be removed in a solid-liquid separation process downstream from the first reactor, such as filtration, as will be described further below. After conducting the sulfidation removal, in certain variations, greater than or equal to about 90% of the initial copper (Cu) present in the liquid stream is removed.

[0183] In another variation, the removal of copper may be achieved via a cementation reaction. In an alternative variation, for a cementation reaction and removal process, iron (Fe) provided from a source of iron (Fe) (9) and a first inorganic base (8) may be added to the liquid stream to precipitate copper (Cu) via a cementation reaction. In certain variations, the first base may be added until a pH of the admixture is about 5 and in certain other variations, about 5.5. While not limiting the present disclosure, it is believed that a

[0188] After conducting the solvent-extraction process, in certain variations, greater than or equal to about 95% of the initial copper (Cu) present in the waste liquid stream and greater than or equal to about 95% of the initial iron (Fe) present in the waste liquid stream may be removed from the waste liquid stream.

[0189] Next, the method may include fluorine removal. The fluorine removal process may further include adding a source of calcium and oxygen (11), for example, calcium oxide, and optionally an oxidant (10) to generate calcium fluoride (CaF_2) that precipitates out of the liquid waste stream. The source of calcium oxide (11) is selected from the group consisting of: lime (CaO), calcium hydroxide ($Ca(OH)_2$), and combinations thereof and the oxidant may comprise hydrogen peroxide (H_2O_2), ozone (O_3), sodium hypochlorite (NaClO), and combinations thereof. In certain variations, solid phase calcium oxide (CaO) or solid phase calcium hydroxide ($Ca(OH)_2$) may be mixed or reacted (*e.g.*, slaked) with water in a reactor or tank to form a liquid phase source of calcium hydroxide ($Ca(OH)_2$) that may then introduced to and/or mixed with the liquid stream to remove fluorine. In certain variations, a pH during the fluoride removal may be greater than or equal to about 1 to less than or equal to about 2. A temperature during the fluorine removal may be about 40°C in certain variations.

[0190] In certain aspects, the oxidant (10) is hydrogen peroxide (H_2O_2). Again, after reaction, the precipitated calcium fluoride (CaF_2) can be removed in a solid-liquid separation process downstream, such as filtration, as will be described further below. Notably, in certain variations, where iron is added to the process (in the reaction above, where copper is precipitated), it may be added to the process prior to lime addition (CaO) for removing fluoride. If unreacted CaO were instead present in the solution, it could

[0194] In certain aspects, after removal of copper and fluoride, the liquid waste stream may be adjusted to have a pH of greater than or equal to about 4.5 to less than or equal to about 5, for example, by adding a base like sodium hydroxide (NaOH) (12). The transition in the pH will assist with removal of remaining impurities, including one or more of iron (Fe), titanium (Ti), aluminum (Al), phosphate (P), and combinations thereof. A temperature during this process may be about 60°C and this mixing may be conducted for about 60 minutes in certain variations.

[0195] The purifying also optionally includes adding a second inorganic base (12) to increase pH of the liquid waste stream to generate one or more metal precipitate compounds comprising a metal selected from the group consisting of: aluminum (Al), titanium (Ti), iron (Fe), and combinations thereof. More specifically, in certain variations, the purifying also optionally includes adding a second inorganic base (12) to increase pH of the liquid waste stream to generate one or more metal hydroxide precipitate compounds selected from the group consisting of: aluminum hydroxide ($Al(OH)_3$), titanium hydroxide ($Ti(OH)_4$), iron phosphate ($FePO_4$), iron hydroxide(s) (either $Fe(OH)_3$ and/or $Fe(OH)_2$), and combinations thereof. In certain variations, the second inorganic base may be added until a pH of the admixture is optionally greater than or equal to about 10.2, optionally greater than or equal to about 10.3, optionally greater than or equal to about 10.4, and in certain aspects, optionally greater than or equal to about 10.5. In certain further variations, the second inorganic base may be added until the pH of the admixture is greater than or equal to about 10.5 to less than or equal to about 11.5, optionally greater than or equal to about 10.5 to less than or equal to about 11, which may depend on the stoichiometry of the metals in the final product to be formed.

interest decreases to less than or equal to about 20 ppm. For example, the solution entering the tank may have impurity levels of 100 to 200 ppm, which may then be reduced to less than about 20 ppm in the purified product stream exiting the solvent extraction tank.

[0202] As shown in Fig. 1, one variation of the inventive technology involves removal of copper (Cu) as an impurity via precipitation involving a cementation reaction where sodium hydroxide (NaOH) is introduced from a source or container (8, 12) and iron (Fe) powder (9) is introduced from a different source or container into the reactor 122 to initiate the removal of impurities such as copper (Cu) via cementation. As will be appreciated by those of skill in the art, while not shown in Fig. 1, the source of sodium hydroxide (NaOH) (8, 12) and the source of iron (Fe) powder (9) may readily be substituted with a single source of sodium sulfide (Na_2S, for example, in water) that is introduced into the reactor 122 when the desired copper (Cu) precipitation reaction is alternatively sulfidation.

[0203] This may be considered a first phase of the impurity removal stage 104. This mixture may be agitated with the agitator 124 for a defined period of time (*e.g.*, 15 minutes, 30 minutes, etc.). In some examples, 19.125 M NaOH and iron (Fe) powder may be added. As noted above, the pH of the leachate solution exiting the leaching reactor 110 and entering the reactor 122 may be acidic, for example, having a pH of greater than or equal to about 0.1 to less than or equal to about 1. In certain examples, pH may be adjusted in the reactor 122 to between greater than or equal to about 1 to less than or equal to about 2 with the use of an inorganic base, like sodium hydroxide (NaOH), to initiate the removal of copper via cementation. For instance, when sodium hydroxide (NaOH) and iron (Fe) powder are added to the leachate for cementation, copper (Cu) precipitate and ferric sulfate (Fe_2SO_4) may be generated. In the alternative variations, where when sodium sulfide

(Na_2S) is added to the leachate for sulfidation, copper (Cu) precipitate in the form of CuS and sulfuric acid (H_2SO_4) may be generated. In some examples, fluorine in the mixture may be converted to hydrogen fluoride (HF). Some of the HF may stay in the solution contained in the reactor 122, while the remainder may be released as a gas (81) and vented to the scrubber 114.

[0204] For example, Cu cementation with zero-valent iron (Fe) may be applied for at least 15 minutes with agitation. During this time, temperature may be maintained at about 60 °C by circulating a heating/cooling medium (*e.g.*, steam, etc.) through the jacket 126 surrounding the reactor 122. Ignoble metals can reduce the noble metal ions according to the electromotive force series. The larger the voltage gap between the two half-cell reactions, the higher the propensity of reaction occurring from a thermodynamic and electrochemistry standpoint. Thus, amongst all the metals available in the leachate, iron and copper may react favorably due to a higher cell potential (E_cell). In the case of the Cu cementation with Fe powder as in the example of Fig. 1, Fe is oxidized to Fe^{2+} and Cu^{2+} is reduced to Cu. The reaction is shown below:

$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$$

[0205] Next, an oxidant from a source or container (10) and a lime component (source of calcium oxide) from a source or container are (11) fed into the reactor 122 to initiate the removal of further impurities such as fluorides from the leachate. This may be considered a second phase of the impurity removal stage 104. For example, the oxidant (10) may be hydrogen peroxide (H_2O_2) as shown in Fig. 1 or another suitable oxidant, and the lime component may be calcium oxide (CaO) or calcium hydroxide ($Ca(OH)_2$) (11) as shown in Fig. 1 or another suitable lime. As discussed above, while not shown, the calcium oxide component may be fed as a liquid

temperature may be maintained at about 60 °C as explained above. This pH transition may assist in the removal of remaining iron, phosphate, titanium, and aluminum. In some embodiments, 19.125M NaOH is added in small doses (*e.g.*, stepwise in increments of 0.5) to gradually increase pH to 5.5. The NaOH added in the third phase may be fed from the NaOH source or container used in the first phase of the stage 104 or a different source or container.

[0212] For example, for iron and phosphate removal, the addition of sulfuric acid (H_2SO_4) to leach the metals encourages the presence of SO_4^{2-}. Hydrogen peroxide (H_2O_2) previously added upstream in the leaching reactor 110 oxidizes ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) ions and thus iron will exist as $Fe_2(SO_4)_3$ in the matrix. In such examples, iron and phosphorus will be precipitated as iron phosphate ($FePO_4$).

[0213] Additionally, iron that was dosed earlier (as Fe powder) for copper removal will facilitate the removal of phosphate PO_4^{3-} as well. Earlier, if cementitious precipitation of copper was conducted, copper (II) cations were reduced to copper metal ($Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$) and iron will oxidize to form ferrous Fe^{2+} ions. Hydrogen peroxide (H_2O_2) used in the leaching reactor 110 oxidizes ferrous Fe^{2+} to ferric Fe^{3+} ions and will remove the PO_4^{3-}as $FePO_4$. In some embodiments, NaOH may be used to adjust the pH and facilitate precipitation of the excess Fe to remove the impurities.

[0214] For titanium and aluminum removal, H_2O_2 acting as an oxidant may push the oxidative states of the metals to titanium (II) and aluminum (III) valences respectively, and the hydroxides may be precipitated out ($Ti(OH)_4$ and $Al(OH)_3$).

[0215] After processing, the impurity removal reactor 122, the liquid waste stream (13) exits reactor 122 and enters through a filter 130 to generate a purified filtrate liquid stream (15)

and a second retentate (14) comprising the one or more metal precipitate compounds and calcium fluoride (CaF_2) that can be further processed in the system as will be described below. Thus, the vessel contents in the reactor 122 are pumped via a pump 128 (*e.g.*, a centrifugal pump, etc.) through filter 130 (*e.g.*, a pressure filter, a hydraulic filter, a gravity filter, etc.), and a second filtrate stream enters the reactor 132 used in the metal recovery stage 106 (sometimes referred to as a co-precipitation stage 106). The pump 128 and the filter 130 are identified as P-002 and F-002, respectively, in Fig. 1. In some embodiments, nearly all impurities (*e.g.*, metallic hydroxides) that precipitated in the reactor 122 are captured in the filter 130.

[0216] After filtration, the impurity removal reactor 122 may be washed with an internal spray ball to remove acid residue in the vessel and to send all reaction products to the reactor (*e.g.*, a receiving reactor) 132. Additionally, any chemical residue in the filter cake may be rinsed to reduce operator exposure during cake collection. Further, a separate water stream may be lined up with the pump 128 and a dilute caustic may be added upstream of the filter 130 to remove residual filtrate, which may be sent to wastewater treatment. At the end this batch cycle (*e.g.*, stage 104), the retentate/hydroxides cake may be collected for disposal.

[0217] After leaching of metals and removal of impurities in the reactors 110, 122, the method may include processing the purified liquid stream to separate and recover nickel (Ni), manganese (Mn), and cobalt (Co) by passing the purified filtrate stream into a metal recovery unit. The metal recovery unity may include a second reactor for conducting a co-precipitation process by increasing pH or one or more chromatographic columns. In certain alternative variations, metal recovery may include both processing a one or more second

reactors and also in one or more chromatographic columns. In this manner, an intermediate liquid stream comprising lithium (Li) and one or more recovered products comprising one or more of nickel (Ni), manganese (Mn), and cobalt (Co) are generated. The one or more recovered products may be an electroactive material precursor, more specifically a positive electrode/cathode active material precursor, having a stoichiometry of $Ni_xMn_yCo_{1-x-y}(OH)_2$, where x is < 1 and y is < 1. To convert this precursor material to an electroactive material (in oxide form), it can be mixed with other reagents, like lithium carbonate for lithiation. After mixing, a thermal treatment like calcination having a temperature of greater than or equal to about 700°C can be performed on the electroactive material precursor to form the electroactive material. In certain variations, the one or more recovered products has a stoichiometry of about $\frac{1}{3}\mathrm{Ni(OH)_2} + \frac{1}{3}\mathrm{Mn(OH)_2} + \frac{1}{3}\mathrm{Co(OH)_2} \rightarrow \mathrm{Ni_{0.33}Mn_{0.33}Co_{0.33}(OH)_2}$, also referred to as NMC111, but may have other stoichiometries, for example, NMC622 (where x is 0.6 and y is 0.2), NMC811 (where x is 0.8 and y is 0.1), and NMC532 (where x is 0.5 and y is 0.3).

[0218] In certain aspects, after leaching of metals and removal of impurities have been conducted as described above, the one or more recovered products comprising one or more of nickel (Ni), manganese (Mn), and cobalt (Co) are extracted from the intermediate liquid stream. In certain variations, a reaction between stoichiometric quantities of transition-metal salts, such as nickel sulfate hydrate ($NiSO_4 \cdot 6H_2O$), manganese sulfate hydrate ($MnSO_4 \cdot H_2O$), and cobalt sulfate hydrate occurs. In one optional variation, a complexing agent (chelating agent) and a base may be used in the process. For example, ammonia (NH_3) may be used as a complexing agent or chelating agent and may be added first to provide a sufficient concentration gradient to promote the formation of $[M(NH_3)]^{2+}$ complexes (where M is a

transition metal like nickel (Ni), manganese (Mn), or cobalt (Co)) prior to particle precipitation. Sodium hydroxide or potassium hydroxide may be selected as the base to maintain a high pH and supply hydroxide ions for metal product precipitation. In such a variation, the reactions that occur are shown below, where "n" represents a number of coordinating ammonia molecules and M represents nickel (Ni), manganese (Mn), or cobalt (Co), which is less than or equal to 6. Reaction (1) shows the metal complexation/chelating into complexes. Reaction (2) shows the addition of a base, like NaOH, that forms metal hydroxides.

$$M^{2+} + nNH_3 \rightarrow [M(NH_3)n]^{2+} \quad (1)$$

$$[M(NH_3)n]^{2+} + 2OH^- \rightarrow M(OH)_2 + nNH_3 \quad (2)$$

In this manner, as will be described further, below, additional processing of the liquid stream can separate and recover nickel (Ni), manganese (Mn), and cobalt (Co) hydroxides.

[0219] In another variation shown in Fig. 1, an NMC electroactive material precursor may be extracted from the system at the reactor 132 in the co-precipitation stage 106. The reactor 132 is identified as V-003 in Fig. 1. Stated in another way, the purified liquid stream (15) is processed in reactor 132 to separate and recover nickel (Ni), manganese (Mn), and cobalt (Co). The purified liquid stream (15) may be received directly from the filter 130 after exiting impurity removal reactor 122 and may be either pretreated as described above with a complexing or chelating agent, like ammonia, or may simply be processed as described herein in reactor 132 to facilitate co-precipitation.

[0220] In terms of electroactive material precursors of interest, $Ni_xMn_yCo_{1-x-y}O_2$ (NMC) layered oxides may now primarily exist as sulfates in the reactor 132 where the liquid stream has not been treated with ammonia. Below is an example of formation of NMC sulfates in the reactor 132 via the use of sulfuric acid (leaching) and hydrogen peroxide as a reductant in stages 102, 104.

$$6LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2\ (s) + 9H_2SO_4(aq) + H_2O_2(aq) \rightarrow 2NiSO_4(aq) +$$

$$2MnSO_4(aq) + 2CoSO_4(aq) + 3Li_2SO_4(aq) + 10H_2O(g) + 2O_2(g)$$

[0221] Thus, the purified filtrate stream comprises nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) and the method according to certain aspects of the present disclosure may include separating nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate stream by passing the purified filtrate stream into the second reactor for conducting the co-precipitation process.

[0222] The co-precipitation process may comprise increasing the pH of the purified filtrate stream to greater than or equal to about 11 in an inert environment (*e.g.*, nitrogen blanket) to form nickel hydroxide hydrate ($Ni(OH)_2 \cdot 6H_2O$), manganese hydroxide hydrate ($Mn(OH)_2 \cdot H_2O$), and cobalt hydroxide hydrate ($Co(OH)_2 \cdot 7H_2O$) that concurrently precipitate from the purified filtrate stream to generate the one or more recovered products.

[0223] Thus, in the co-precipitation stage 106, sodium hydroxide (NaOH) (19) may be fed into the reactor 132 to increase the pH level, as shown in Fig. 1. For example, 19.125M NaOH may be added to increase the pH to approximately 10.5, 11, etc. During this time, the solution in the reactor 132 may be agitated with the agitator 134 for a defined period of time (*e.g.*, about 30 minutes, etc.), and the temperature may be maintained at about 80 °C (176 °F) by circulating a heating/cooling medium through the jacket 136 surrounding the reactor 132. After the agitation period is complete, $NiMnCo(OH)_6$ precipitate, sodium sulfate, and lithium sulfate are generated as further explained below.

[0224] For example, after NaOH (19) is added to the reactor 132, the metal sulfates $NiSO_4$, $MnSO_4$, and $CoSO_4$ are converted into their hydroxides, forming nickel hydroxide hydrate ($Ni(OH)_2 \cdot 6H_2O$), manganese hydroxide hydrate ($Mn(OH)_2 \cdot H_2O$), and cobalt

[0228] The method may further comprise determining a first ratio of Ni:Mn:Co in the purified filtrate stream prior to the co-precipitation process. The method may include comparing the first ratio to a target stoichiometric ratio of Ni:Mn:Co for the one or more recovered products. The method may then include adding one or more of nickel sulfate ($NiSO_4$) (16), manganese sulfate ($MnSO_4$) (17), and cobalt sulfate ($CoSO_4$) (18) to the purified filtrate stream to adjust an amount of nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) prior to adjusting the pH. In this manner, the one or more recovered products has a second ratio corresponding to the target stoichiometric ratio.

[0229] Thus, where the Ni:Mn:Co values may not suffice for an intended recycled electroactive material precursor, or should the desired product be of different NMC permutation/stoichiometry, the sulfates may be added as necessary to the reactor 132, as show in Fig. 1. This may achieve, for example, molar equivalence between nickel, manganese, and cobalt in the reactor 132. Below is one such example formulation of adding NMC sulfates. In certain aspects, the system may include an analyser unit that can sample the purified liquid stream and determine a content of nickel (Ni), manganese (Mn), and cobalt (Co) upstream of the reactor. The co-precipitation unit may also comprise a controller and one or more metering pumps to regulate flow of a nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) into the plurality of inlets of the third heated reactor. The controller receives input from the analyzer and controls the one or more metering pumps to adjust the amount of respective sulfates fed to the stream or into the reactor.

[0230] In various embodiments, NMC sulfates may be dosed accordingly via the use of automated process implementing a controller such as a programmable logic

convenience for the entire end user and management by dosing the appropriate nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) to supplement the necessary concentrations of Ni, Mn, and Co in the solution to produce the appropriate NMC hydroxide permutation (and/or for other permutations, such as NMC622, NMC811, NMC532, by way of non-limiting example).

[0233] With continued reference to Fig. 1 and/or Fig. 2, after adding the appropriate amount of NaOH (19) and the appropriate amounts of NMC sulfates (if necessary from 16, 17, 18), the reactor 132 contains all of the N-M-C product as precipitate, as well as sodium sulfate and lithium sulfate that are dissolved under process conditions, as explained above. In some embodiments, residual HF in the solution contained in the reactor 132 may be released as a gas (82) and vented to the scrubber 114. The contents in the reactor 132 are then pumped via a pump 138 (*e.g.*, a centrifugal pump, etc.) through a filter 140 (*e.g.*, a pressure filter, a hydraulic filter, a gravity filter, etc.), and a third filtrate (*e.g.*, including sodium sulfate and lithium sulfate) (20) is collected in the reactor (*e.g.*, a receiving reactor) 142 used in the precipitation stage 108. The retentate (21) from the filter 140 includes the one or more recovered products comprising nickel (Ni), manganese (Mn), and cobalt (Co). The pump 138 and the filter 140 are identified as P-003 and F-003, respectively, in Fig. 1. In some embodiments, nearly all of the one or more recovered products (*e.g.*, NMC product) that precipitated in the reactor 132 are captured as retentate in the filter 140.

[0234] After filtration, the reactor 132 may be washed with an internal spray ball to remove any process fluid residue in the reactor 132 and to send all reaction products to the reactor 142. At the end this batch cycle (stage 106), the product NMC cake may be collected for further drying and packaging.

[0235] In some embodiments, at least some water in the contents passing through the filter 140 (*e.g.,* the third filtrate) (22) may be removed before collecting in the reactor 142. This may be accomplished through heating and distillation/evaporation processes. In various embodiments, the process to remove water from the third filtrate may be considered as part of the co-precipitation stage 106 and/or the precipitation stage 108. In other embodiments, the process to remove water from the third filtrate may be considered a separate stage such as a water removal stage.

[0236] For example, in Fig. 1, the third filtrate (22) including sodium sulfate and lithium sulfate is passed through an evaporator 144. The evaporator separates the intermediate third filtrate stream into a concentrate stream (26) and a distillate stream (25). In such examples, about 50% of the water in the filtrate may be evaporated and form the distillate stream and the resulting concentrate steam may be collected in a storage tank. In some cases, the collected distillate stream (25) may be used in upstream processes if desired. The remaining contents (*e.g.*, a concentrate stream) (26) may then be pumped via a pump 146 to the reactor 142. The pump 146 is identified as P-301 in Fig. 1. In some embodiments, the concentrate stream may be collected in another storage tank before being pumped to the reactor 142. In certain aspects, the lithium concentration is increased for the next process step, for example only, after being processed in the evaporator a concentration of lithium (Li) may be greater than about 12 g/L in the stream.

[0237] The methods of the present disclosure also contemplate introducing the intermediate liquid stream, for example, the concentrate stream (26) into a lithium precipitation reactor to precipitate at least one compound comprising lithium (Li). For example, the concentrate stream may be introduced into a lithium precipitation reactor. Next, sodium

carbonate (Na_2CO_3) (28) may be added along with inorganic base (*e.g.*, NaOH) (27) to the lithium precipitation reactor. The liquid stream has a temperature of greater than or equal to about 80°C to less than or equal to about 90°C for greater than or equal to about 90 minutes while in the lithium precipitation reactor to generate lithium carbonate (Li_2CO_3) precipitate.

[0238] In the precipitation stage 108, sodium carbonate (Na_2CO_3) (28) is optionally fed into a lithium precipitation reactor 142 to convert lithium sulfate (Li_2SO_4) into lithium carbonate (Li_2CO_3). The reactor 142 is identified as V-004 in Fig. 1. During this time (or before), the temperature of the contents (*e.g.*, the concentrate stream, the third filtrate, etc.) in the reactor 142 may be adjusted to a desired temperature (*e.g.*, about 80 °C - 90 °C) by circulating a heating/cooling medium through the jacket 150 that serves as a heat exchanger. In one variation, the sodium carbonate (Na_2CO_3) solution may be added to the liquid stream comprising lithium in the lithium precipitation reactor at a feed rate of 20 L/minute.

[0239] Next, sodium hydroxide (NaOH) (27) is optionally fed into the reactor 142 to increase the pH level, as shown in Fig. 1. For example, 19.125M of NaOH may be added to increase the pH to approximately 13. During this time, the solution in the reactor 142 may be agitated with the agitator 134 for a defined period of time (*e.g.*, about 30 minutes, 1 hour, 1.5 hours, etc.), and the temperature may be maintained at the desired temperature with the jacket 150. After the agitation period is complete, the lithium sulfate will precipitate as lithium carbonate Li_2CO_3, shown in the example reactions (either (3) and/or (4) and (5)) below:

$$Li_2SO_4\ (aq) + Na_2CO_3 \rightarrow Li_2CO_3\ (s) + Na_2SO_4\ (aq) \quad (3)$$

$$Li_2SO_4 + 2NaOH \rightarrow 2LiOH + Na_2SO_4 \text{ (during co-precipitation)} \quad (4)$$

$$2LiOH + Na_2CO_3 \rightarrow Li_2CO_3 + 2NaOH \quad (5)$$

[0240] The vessel contents (29) in the reactor 142 are then pumped via a pump 152 (*e.g.,* a centrifugal pump, etc.) through a filter 154 (*e.g.,* a pressure filter, a hydraulic filter, a gravity filter, etc.). The pump 152 and the filter 154 are identified as P-004 and F-004, respectively, in Fig. 1. In some embodiments, nearly all the lithium carbonate product (30) may be captured in the filter 154. After filtration, the reactor 142 may be washed with an internal spray ball to remove any process fluid residue in the reactor 142. At the end this batch cycle (*e.g.,* stage 108), the product Li_2CO_3 cake (30) may be collected for further drying and packaging. In various embodiments, the effluent (*e.g.,* a fourth filtrate) (31) passing through the filter 154 may be sent to wastewater treatment and/or recycled back to the reactor 110 to facilitate dilution of acid and magnify lithium concentration in a subsequent performed process conducted in system 100.

[0241] In various embodiments, the contents from the reactor 132 of Fig. 1 may be provided to another suitable module instead of the evaporator 144 before collecting in the reactor 142. For example, in some cases, where volumetric applications of 10 m^3 and above are processed, the evaporator may provide limited capacities. As such, in some embodiments, the contents may pass through a thermal shock module coupled with electrode ionization to facilitate thermal shocking by lowering temperatures. In certain variations, a temperature after the thermal shock process may be less than or equal to about 30°C, optionally less than or equal to about 25°C, and in certain aspects, greater than or equal to about 0°C to less than or equal to about 30°C, optionally greater than or equal to about 0°C to less than or equal to about 25°C. In such examples, a thermal shocking process

may be less costly, less energy intensive and less time consuming as compared to an evaporation process.

[0242] In one variation, the thermal shock module is advantageous where the intermediate liquid stream comprises lithium sulfate (Li_2SO_4) and sodium sulfate (Na_2SO_4). Prior to introducing the stream into the lithium precipitation reactor, the intermediate liquid stream is subjected to a thermal shock process followed by ionization in an electrode ionization unit to facilitate precipitation of sodium sulfate (Na_2SO_4) from the intermediate liquid stream. Sodium sulfate has lower solubility than lithium sulfate, thus desirably removing the sodium sulfate from solution. This may be followed by adding sodium carbonate (Na_2CO_3) into the lithium precipitation reactor to generate lithium carbonate (Li_2CO_3) precipitate.

[0243] For example, Fig. 3 illustrates a process that occurs in system 300 substantially similar to the process conducted in system 100 of Fig. 1, but where the contents passing through the filter 140 (*e.g.*, the third filtrate) (22) are passed through a thermal shock module 302 and an electrode ionization module 304. The process conducted in system 300 includes the stages 102, 104, 106, 108 of Fig. 1 where contents are collected and processed in the reactors 110, 122, 132, 142 (also identified as E-82, E-83, E-84, E-78, respectively, in Fig. 3) and pumped via pumps 118, 128, 138, 146, 152 (E-74, E-69, E,72, E-77, E-70, and E-81, respectively, in Fig. 3). In various embodiments, processes completed with the modules 302 and/or 304 may be considered as part of the co-precipitation stage 106 and/or the precipitation stage 108. In other embodiments, such processes may be considered a separate stage.

[0244] In the example of Fig. 3, the contents (22) from the filter 140 are passed to the thermal shock module (*e.g.*, a freeze crystallizer module) 302 to precipitate sodium sulfate (23)

from the lithium sulfate/sodium sulfate stream. In the module 302, lithium sulfate may be extracted from the solution containing sodium cations and sulfate anions. For example, monovalent cationic precipitation may be difficult in heating and distillation/evaporation processes due to their high solubility product and solubility in waters. However, in the module 302, the lithium sulfate/sodium sulfate solution undergoes a thermal shock to lower the temperature of both precipitates. Since sodium sulfate has a lower solubility product than lithium sulfate, more sodium sulfate may be removed as precipitate after the thermal shock.

[0245] Next, the remaining solution (24) is pumped via a pump 306 to the electrode ionization module 304 (also identified as E-79 in Fig. 3) via to remove water (25) from the solution and generate a precipitate/sludge including lithium sulfate (26). The precipitate and its sludge (26) may be collected as a main product while permeate water (25) may be collected and recycled back to the reactor 110 to facilitate dilution of acid. This may magnify the lithium concentration in the remaining sludge. The main product (*e.g.*, the precipitate and its sludge) including lithium sulfate (26) is then pumped via the pump 146 to the reactor 142 where sodium carbonate (28) is added to precipitate the lithium sulfate as lithium carbonate as explained above.

[0246] The method also contemplates separating by a chromatographic separation process rather than or in addition to a co-precipitation process. The method may include passing the purified filtrate stream in a first direction in a chromatographic column or packed-bed column/reactor comprising a chelating resin to conduct a chromatographic separation process. In certain variations, the pH in the column may be less than or equal to about 4.5. After passing through the chromatographic column or packed-bed column/reactor, a raffinate stream comprising at least one manganese (Mn)-containing

(KOH), lithium hydroxide (LiOH) and the like to forming an intermediate liquid stream. The manganese hydroxide ($Mn(OH)_2$) may then be removed or separated from the stream before entering the lithium precipitation reactor. In certain aspects, manganese hydroxide ($Mn(OH)_2$) thus formed may be later combined with the at least one compound comprising lithium (Li), for example, lithium carbonate (Li_2CO_3), to form $LiMnO_4$ electroactive material.

[0261] The methods may also further comprise adjusting the pH of the purified filtrate stream by adding sodium hydroxide (NaOH) to the purified filtrate stream to have a pH of about 2.5 and adjusting the pH of the first raffinate stream by adding sodium hydroxide (NaOH) to the first raffinate stream to have a pH of about 3.5.

[0262] In certain variations, the stationary phase in the first chromatographic column or packed-bed column/reactor and the stationary phase in the second chromatographic column or packed-bed column/reactor are any resin with selectivity for manganese (Mn) ions, nickel (Ni) ions, and/or cobalt (Co) ions and in particular, nickel (Ni) ions and/or cobalt (Co) ions known in the art. In one variation, the stationary phase in the first chromatographic column or packed-bed column/reactor comprises macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid and a stationary phase in the second chromatographic column or packed-bed column/reactor comprises macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid.

[0263] For example, Fig. 5 illustrates yet another chromatographic separation process conducted in system 500 that may be implemented with the systems 100, 300 of Figs. 1 and 3, where leachate from an impurity removal stage (*e.g.*, the impurity removal

CLAIMS

What is claimed is:

1. A process for recovering metals from a lithium-ion battery waste stream, the process comprising:

purifying a lithium-ion battery waste liquid stream comprising sulfuric acid (H_2SO_4) in a first reactor to remove fluorine (F), phosphate (P), and one or more impurity metals selected from the group consisting of: copper (Cu), aluminum (Al), iron (Fe), and titanium (Ti), wherein the purifying includes:

(i) removing copper (Cu) from the waste liquid stream;

(ii) adding a source of calcium oxide and an oxidant to generate calcium fluoride (CaF_2) that precipitates out of the waste liquid stream; and

(iii) adding a first inorganic base to increase pH of the waste liquid stream to generate one or more metal precipitate compounds selected from the group consisting of: aluminum hydroxide ($Al(OH)_3$), titanium hydroxide ($Ti(OH)_4$), iron phosphate ($FePO_4$), and one or more iron hydroxides;

passing the waste liquid stream exiting the first reactor through a filter to generate a purified filtrate liquid stream and a second retentate comprising the one or more metal precipitate compounds, copper (Cu), and calcium fluoride (CaF_2);

separating nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate liquid stream by passing the purified filtrate liquid stream into one or more of:

(i) a second reactor for conducting a co-precipitation process by increasing pH; or

(ii) one or more chromatographic columns;

to generate an intermediate liquid stream comprising lithium (Li) and one or more recovered products comprising one or more of nickel (Ni), manganese (Mn), and cobalt (Co) that are removed from the intermediate liquid stream; and

introducing the intermediate liquid stream into a lithium precipitation reactor to precipitate at least one compound comprising lithium (Li).

2. The process of claim 1, wherein the removing copper (Cu) from the waste liquid stream comprises:

(i) precipitating copper (Cu) by adding a source of iron (Fe) and a second inorganic base to the waste liquid stream to precipitate copper (Cu) via a cementation reaction;

(ii) adding a source of sodium sulfide (Na_2S) to the waste liquid stream to precipitate copper (Cu) via a sulfidation reaction; or

(iii) subjecting the waste liquid stream to a solvent-extraction process by mixing the waste liquid stream with an extractant and an organic phase to remove copper (Cu).

3. The process of claim 2, wherein the removing copper (Cu) from the waste liquid stream comprises:

the (i) precipitating copper (Cu) via the cementation reaction and the source of iron (Fe) comprises iron powder, the first inorganic base and the second inorganic base each comprise sodium hydroxide (NaOH), the source of calcium oxide is selected from the group consisting of: lime (CaO), calcium hydroxide ($Ca(OH)_2$), and combinations thereof, and the oxidant is selected from the group consisting of: hydrogen peroxide (H_2O_2), ozone (O_3), sodium hypochlorite (NaClO), and combinations thereof, wherein

the second inorganic base is added until pH is about 5, the first inorganic base is added until pH is about 10.5, and the oxidant comprises hydrogen peroxide (H_2O_2) which is added at a concentration of greater than or equal to about 4 % by volume to less than or equal to about 6% by volume of total liquid contents; optionally

the adding the source of iron (Fe) and the second inorganic base to the waste liquid stream is conducted at a pH of greater than or equal to about 1 to less than or equal to about 2 while mixing for a duration of greater than or equal to about 15 minutes at a temperature of greater than or equal to about 55°C to less than or equal to about 65°C; or

optionally

about 2.5 g of iron powder is added for each liter (L) of the waste liquid stream.

4. The process of claim 1, wherein the removing copper (Cu) from the waste liquid stream comprises the (ii) adding a source of sodium sulfide (Na_2S) to the waste liquid stream to precipitate copper (Cu) via a sulfidation reaction.

5. The process of claim 1, wherein the removing copper (Cu) from the waste liquid stream comprises the (iii) subjecting the waste liquid stream to a solvent-extraction process by mixing the waste liquid stream with an extractant and an organic phase to remove copper (Cu); wherein optionally

the extractant comprises 2-hydroxy-5-nonylbenzaldehyde oxime and the organic phase comprises kerosene.

6. The process of any one of the previous claims, wherein the purifying further includes introducing a source of phosphate to the waste liquid stream prior to the first inorganic base to increase pH of the waste liquid stream so as to generate aluminum phosphate ($AlPO_4$) precipitate;

wherein optionally the source of phosphate comprises sodium phosphate (Na_3PO_4).

7. The process of any one of the previous claims, wherein the adding the source of calcium oxide and the oxidant to generate calcium fluoride (CaF_2) is conducted at a pH of greater than or equal to about 1 to less than or equal to about 2 while mixing for a duration of greater than or equal to about 30 minutes at a temperature of greater than or equal to about 55°C to less than or equal to about 65°C.

8. The process of any one of the previous claims, wherein the adding of the first inorganic base increases the pH of the waste liquid stream to greater than or equal to about 4 to less than or equal to about 5;

wherein optionally the adding of the first inorganic base to increase pH is conducted while mixing for a duration of greater than or equal to about 60 minutes at a temperature of greater than or equal to about 55°C to less than or equal to about 65°C.

9. The process of any one of the previous claims, wherein the purified filtrate liquid stream comprises nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) and the separating nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate liquid stream occurs by passing the purified filtrate liquid stream into the second reactor for conducting the co-precipitation process that comprises:

increasing the pH of the purified filtrate liquid stream to greater than or equal to about 11 in an inert environment to form nickel hydroxide hydrate ($Ni(OH)_2 \cdot 6H_2O$), manganese hydroxide hydrate ($Mn(OH)_2 \cdot H_2O$), and cobalt hydroxide hydrate ($Co(OH)_2 \cdot 7H_2O$) that concurrently precipitate from the purified filtrate liquid stream to generate the one or more recovered products,

wherein optionally the increasing the pH of the purified filtrate liquid stream further comprises first adding ammonia to the purified liquid stream that comprises nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$).

10. The process of any one of the previous claims, wherein the one or more recovered products is an electroactive material precursor having a stoichiometry of $Ni_xMn_yCo_{1-x-y}(OH)_2$, where x is < 1 and y is < 1; optionally.

the one or more recovered products has a stoichiometry of about $\frac{1}{3}Ni(OH)_2 + \frac{1}{3}Mn(OH)_2 + \frac{1}{3}Co(OH)_2 \rightarrow Ni_{0.33}Mn_{0.33}Co_{0.33}(OH)_2$;

optionally the process further comprises

determining a first ratio of Ni:Mn:Co in the purified filtrate liquid stream prior to the co-precipitation process;

comparing the first ratio to a target stoichiometric ratio of Ni:Mn:Co for the one or more recovered products; and

adding one or more of nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) to the purified filtrate liquid stream to adjust an amount of nickel sulfate ($NiSO_4$), manganese sulfate ($MnSO_4$), and cobalt sulfate ($CoSO_4$) prior to adjusting the pH so that the one or more recovered products has a second ratio corresponding to the target stoichiometric ratio.

11. The process of any one of the previous claims, wherein the separating occurs by passing the purified filtrate liquid stream in a first direction in a chromatographic column comprising a chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 4.5 that generates a raffinate stream comprising at least one manganese (Mn)-containing species and at least one lithium (Li)-containing species

that exits the chromatographic column, while nickel (Ni) ions and cobalt (Co) ions are retained on the chelating resin in the chromatographic column; and

regenerating the chromatographic column by passing a regeneration liquid having a pH of less than or equal to about 1.5 in the chromatographic column to form an extract stream comprising the nickel (Ni) ions and cobalt (Co) ions; and

precipitating nickel hydroxide ($Ni(OH)_2$) and cobalt hydroxide ($Co(OH)_2$) from the extract stream; wherein optionally

the method further comprises forming an electroactive material precursor by combining nickel hydroxide ($Ni(OH)_2$) and cobalt hydroxide ($Co(OH)_2$) with aluminum hydroxide ($Al(OH)_3$) and at least one compound comprising lithium (Li); optionally the

process further comprises adjusting the pH of the purified filtrate liquid stream to be greater than or equal to about 4 to less than or equal to about 5 as it enters the chromatographic column, wherein the process further comprises precipitating manganese hydroxide ($Mn(OH)_2$) by adjusting pH to be greater than or equal to about 8 to less than or equal to about 10 thus forming the intermediate liquid stream and further separating the manganese hydroxide ($Mn(OH)_2$) from the intermediate liquid stream; or precipitating manganese dioxide (MnO_2) by conducting one or more of: adding sodium permanganate or potassium permanganate to the raffinate stream, and subjecting the raffinate stream to ozonation;

optionally the adjusting the pH comprises adding sodium hydroxide (NaOH) to the purified filtrate liquid stream; or

optionally a stationary phase in the one or more chromatographic columns comprises a macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid.

12. The process of any one of the previous claims 1 to 11, wherein the separating occurs by passing the purified filtrate liquid stream in a first direction in a first chromatographic column comprising a first chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 1.5 that generates a first raffinate stream comprising at least one manganese (Mn)-containing species, at least one cobalt (Co)-containing species, and at least one lithium (Li)-containing species that exits the first chromatographic column, while nickel (Ni) ions are retained on the first chelating resin in the first chromatographic column;

passing the first raffinate stream in a first direction in a second chromatographic column comprising a second chelating resin to conduct a chromatographic separation process at a pH of less than or equal to about 2.5 that generates a second raffinate stream comprising at least one manganese (Mn)-containing species and at least one lithium (Li)-containing species that exits the second chromatographic column, while cobalt (Co) ions are retained on the second chelating resin in the second chromatographic column;

regenerating the first chromatographic column by passing a first regeneration liquid having a pH of less than or equal to about 1.5 in the first chromatographic column to form a first extract stream comprising the nickel (Ni) ions;

precipitating nickel hydroxide ($Ni(OH)_2$) from the first extract stream;

regenerating the second chromatographic column by passing a second regeneration liquid having a pH of less than or equal to about 2.5 in the second chromatographic column to form a second extract stream comprising the cobalt (Co) ions; and

precipitating cobalt hydroxide ($Co(OH)_2$) from the second extract stream;

optionally the process further comprises forming an electroactive material precursor by combining nickel hydroxide ($Ni(OH)_2$) and cobalt hydroxide ($Co(OH)_2$) with aluminum hydroxide ($Al(OH)_3$) and the at least one compound comprising lithium (Li);

optionally the process further comprises precipitating manganese hydroxide ($Mn(OH)_2$) from the second raffinate stream by adjusting pH to be greater than or equal to about 8 to less than or equal to about 10 thus forming the intermediate liquid stream and separating the manganese hydroxide ($Mn(OH)_2$);

optionally the at least one compound comprising lithium (Li) comprises lithium carbonate (Li_2CO_3) that is combined with manganese hydroxide ($Mn(OH)_2$) to form lithium manganese oxide (LMO) electroactive material;

optionally the process further comprises adjusting the pH of the purified filtrate liquid stream by adding sodium hydroxide (NaOH) to the purified filtrate liquid stream to have a pH of about 2.5 and adjusting the pH of the first raffinate stream by adding sodium hydroxide (NaOH) to the first raffinate stream to have a pH of about 3.5; or wherein optionally

a stationary phase in the first chromatographic column comprises macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid and a stationary phase in the second chromatographic column comprises macroporous styrene divinylbenzene having functional groups comprising iminodiacetic acid.

13. The process of any one of the previous claims, wherein the at least one compound comprising lithium (Li) comprises lithium carbonate (Li_2CO_3) that is combined with manganese oxide ($Mn(OH)_2$) to form lithium manganese oxide (LMO) electroactive material.

14. The process of any one of the previous claims, wherein the lithium-ion battery waste stream is black mass and prior to the purifying, the process further comprises:

generating the lithium-ion battery waste liquid stream by subjecting the black mass to a leaching process that comprises:

mixing an inorganic acid with the black mass to form an acidic admixture;

mixing an oxidant with the acidic admixture; and

adding deionized water to the acidic admixture; and

passing a leachate stream through a second filter to generate a filtrate liquid stream comprising one or more metal sulfates and a first retentate comprising graphite;

wherein optionally both the mixing of the inorganic acid and the mixing of the oxidant are conducted at a temperature of less than or equal to about 100°C;

optionally the inorganic acid comprises sulfuric acid (H_2SO_4), the oxidant comprises hydrogen peroxide (H_2O_2), and a pH of the acidic admixture is less than or equal to about 2.5;

optionally the mixing the inorganic acid comprises adding black mass to the sulfuric acid (H_2SO_4) having a molarity of about 4M, the mixing the oxidant comprises adding about 30% by mass hydrogen peroxide (H_2O_2) to the acidic admixture so that the acidic admixture has a solid/liquid ratio of 100 g/L, followed by mixing for greater than or equal to about 2 hours, and then the adding of the deionized water dilutes the sulfuric acid

(H_2SO_4) to a molarity of about 2M, followed by mixing for greater than or equal to about 30 minutes.

15. The process of claim 13, wherein the one or more recovered products have a purity level of greater than or equal to about 95% and comprise less than or equal to about 5% by mass of a total cumulative amount of impurities comprising aluminum (Al), copper (Cu), iron (Fe), phosphorus (P), titanium (Ti) and fluorine (F);

optionally the one or more recovered products have a purity level of greater than or equal to about 98% and comprise less than or equal to about 2% by mass of a total cumulative amount of impurities comprising aluminum (Al), copper (Cu), iron (Fe), phosphorus (P), titanium (Ti) and fluorine (F); or

optionally the separating recovers greater than or equal to about 80% by mass of each of nickel (Ni), manganese (Mn), and cobalt (Co) from the purified filtrate liquid stream.

16. The process of any one of claims 13 to 14, wherein prior to the introducing the intermediate liquid stream into the lithium precipitation reactor, subjecting the intermediate liquid stream to a solvent-extraction process by mixing the waste liquid stream with an extractant and an organic phase to remove impurities comprising a metal selected from the group consisting of: copper (Cu), iron (Fe), aluminum (Al), and combinations thereof;

wherein optionally the extractant comprises bis-(2-ethylhexyl) phosphoric acid and the organic phase comprises kerosene.

17. The process of any one of claims 1 to 16, wherein the introducing the intermediate liquid stream into a lithium precipitation reactor comprises adding sodium

carbonate (Na_2CO_3) and a second inorganic base to the lithium precipitation reactor, wherein the intermediate liquid stream has a temperature of greater than or equal to about 80°C to less than or equal to about 90°C for greater than or equal to about 90 minutes to generate lithium carbonate (Li_2CO_3) precipitate;

optionally the intermediate liquid stream comprises lithium sulfate (Li_2SO_4) and sodium sulfate (Na_2SO_4) and prior to the introducing, the intermediate liquid stream is subjected to a thermal shock process so that a temperature is greater than or equal to about 0°C to less than or equal to about 30°C followed by ionization in an electrode ionization unit to facilitate precipitation of sodium sulfate (Na_2SO_4) from the intermediate liquid stream, followed by adding sodium carbonate (Na_2CO_3) into the lithium precipitation reactor to generate lithium carbonate (Li_2CO_3) precipitate.

18. The process of any one of claims 13 to 17, wherein a separation efficiency for each of copper (Cu), aluminum (Al), titanium (Ti), and iron (Fe) is respectively greater than or equal to about 95% and a separation efficiency for fluorine is greater than or equal to about 80%.