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(54) **PROCESS FOR SEPARATION OF AT LEAST ONE METAL SULFIDE FROM A MIXED SULFIDE ORE OR CONCENTRATE**

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*15/0065* (2013.01)

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(60) Provisional application No. 61/934,193, filed on Jan. 31, 2014.

(57)

**ABSTRACT**

A stabilization process for an arsenic solution comprising thiosulfates, the process comprising: acidifying the arsenic solution to decompose the thiosulfates, to yield an acidified solution; oxidizing the acidified solution to oxidize residual As<sup>3+</sup> to As<sup>5+</sup> and reduced sulfur species to sulfates, to yield a slurry comprising elemental sulfur; separating elemental sulfur from the slurry to yield a liquid; oxidizing the liquid to oxidize residual reduced sulfur species, to yield an oxidized solution; and forming a stable arsenic compound from the oxidized solution.

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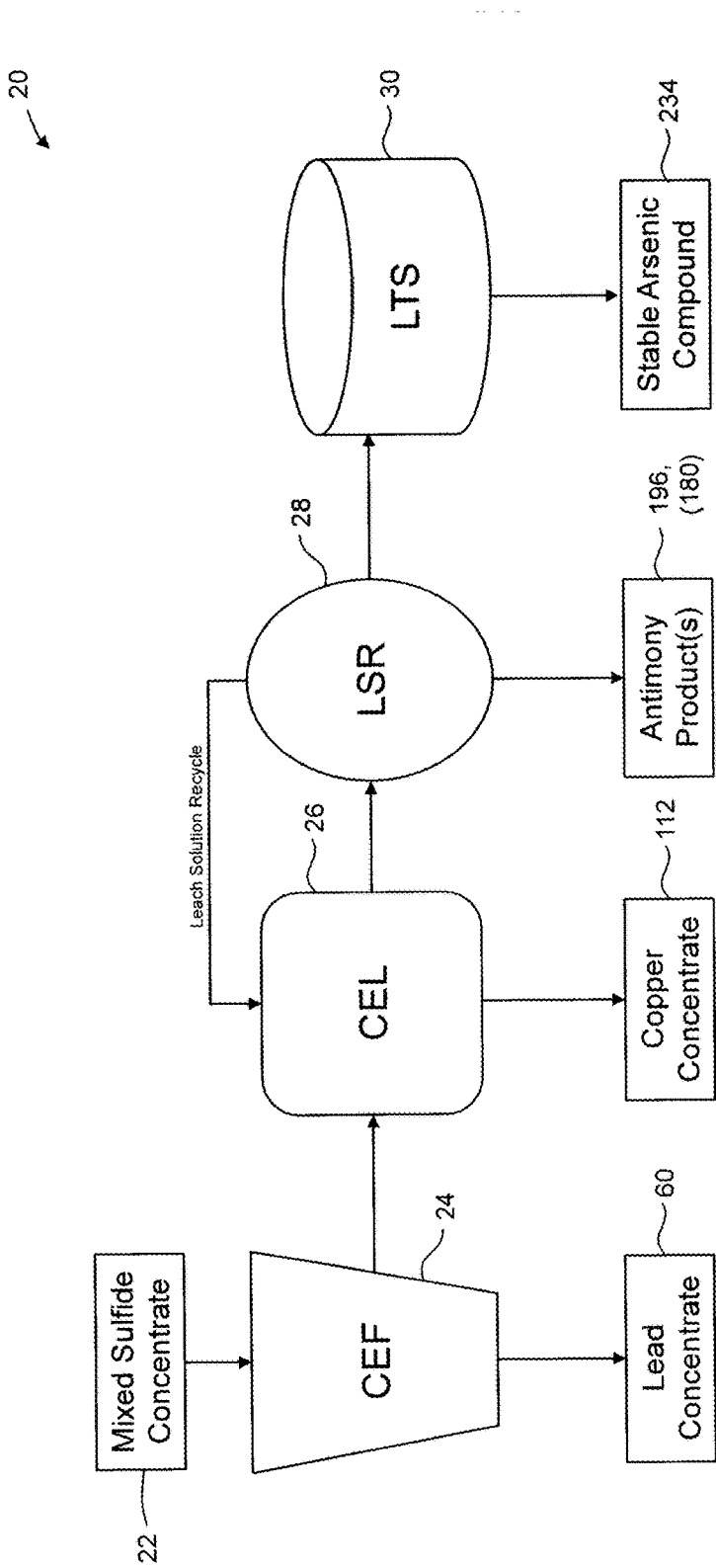


Figure 1

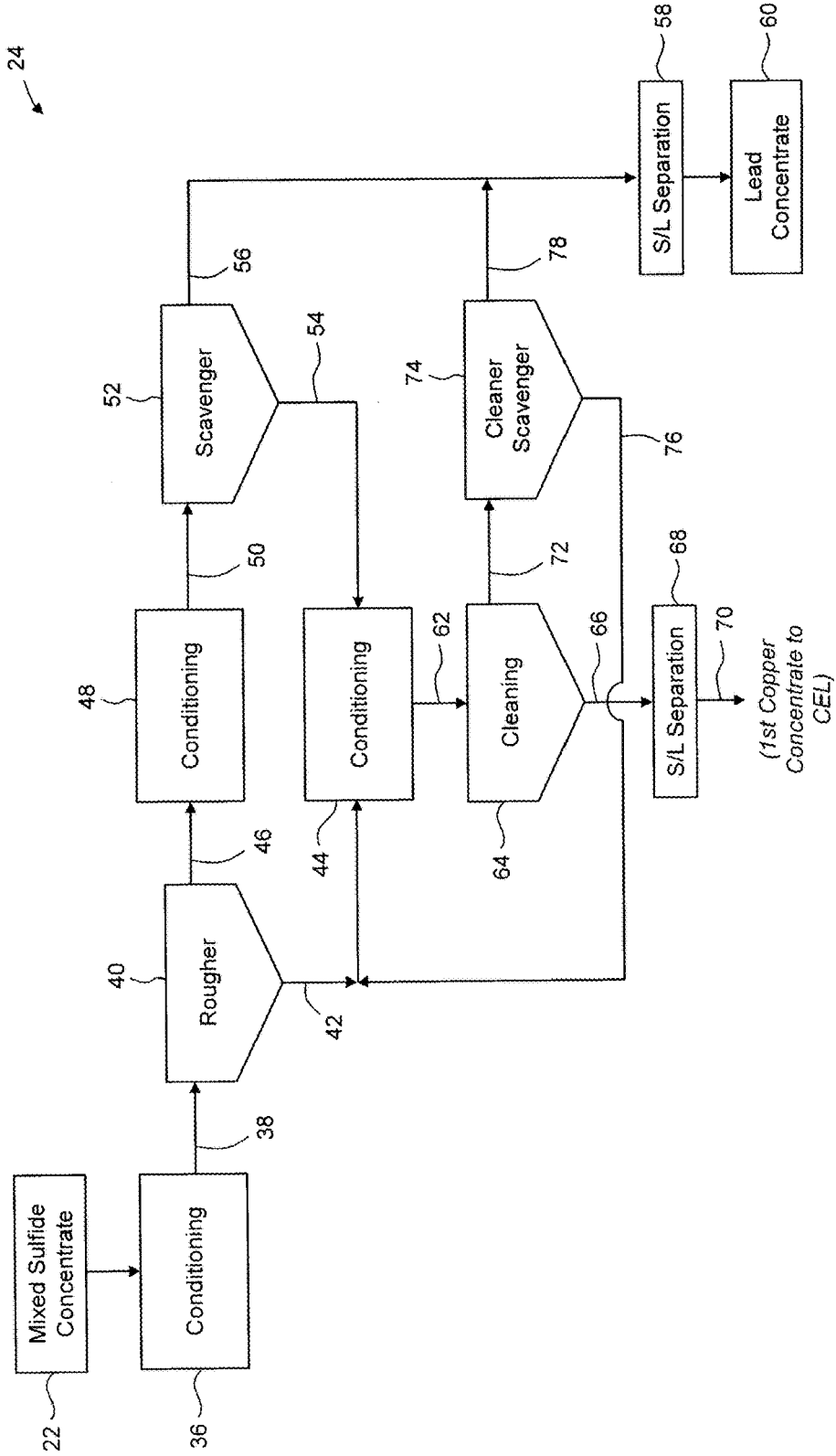


Figure 2

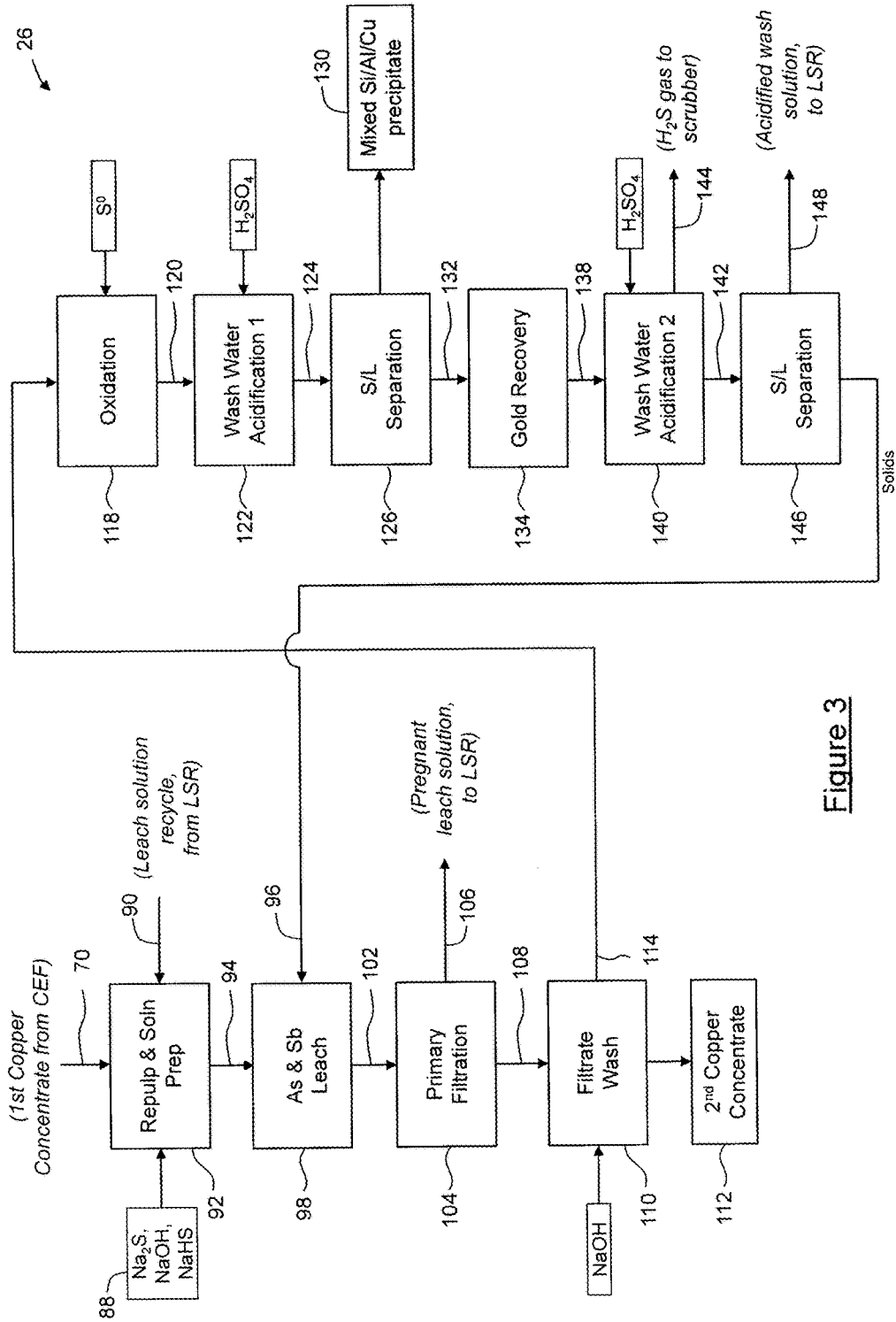


Figure 3

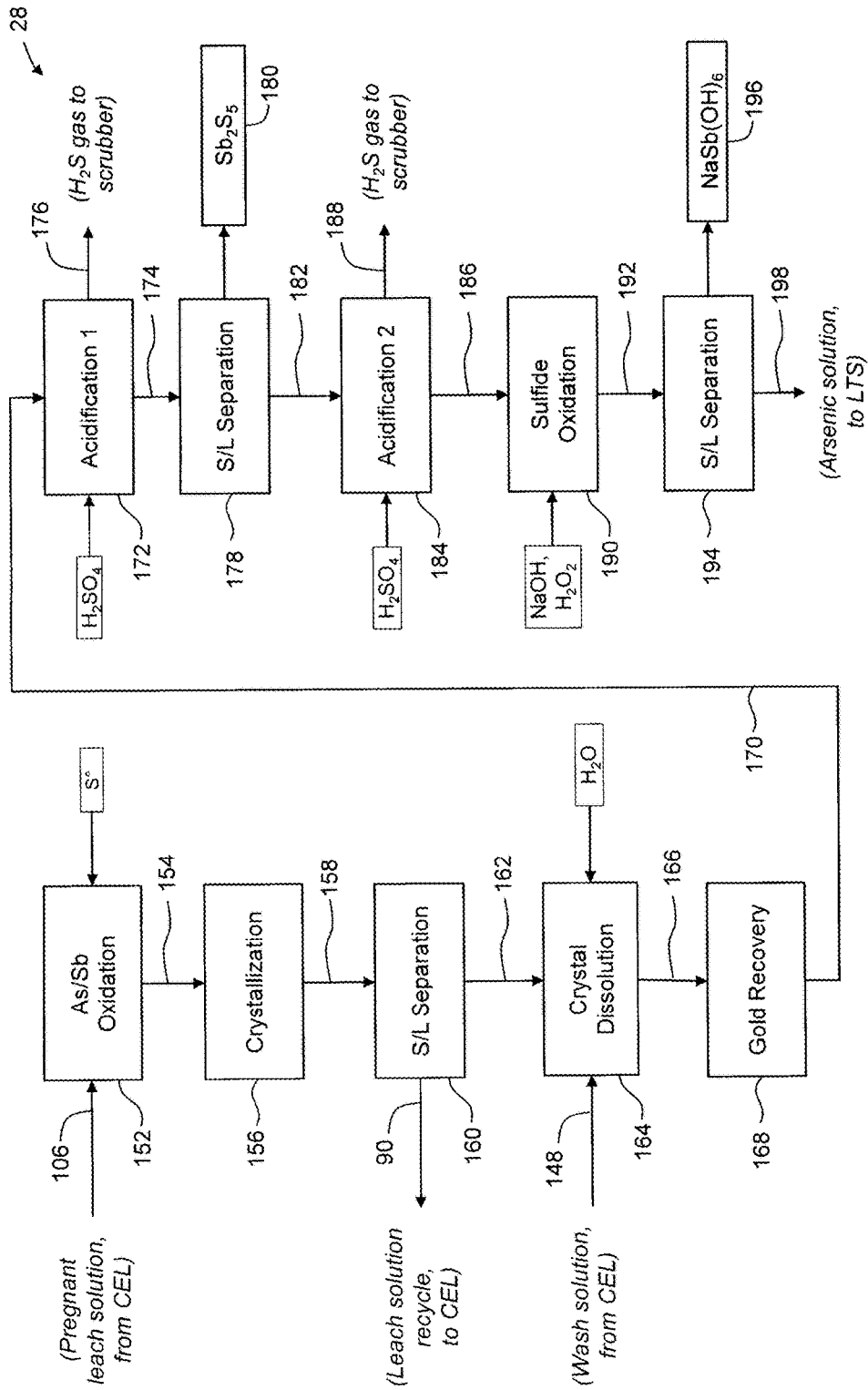


Figure 4

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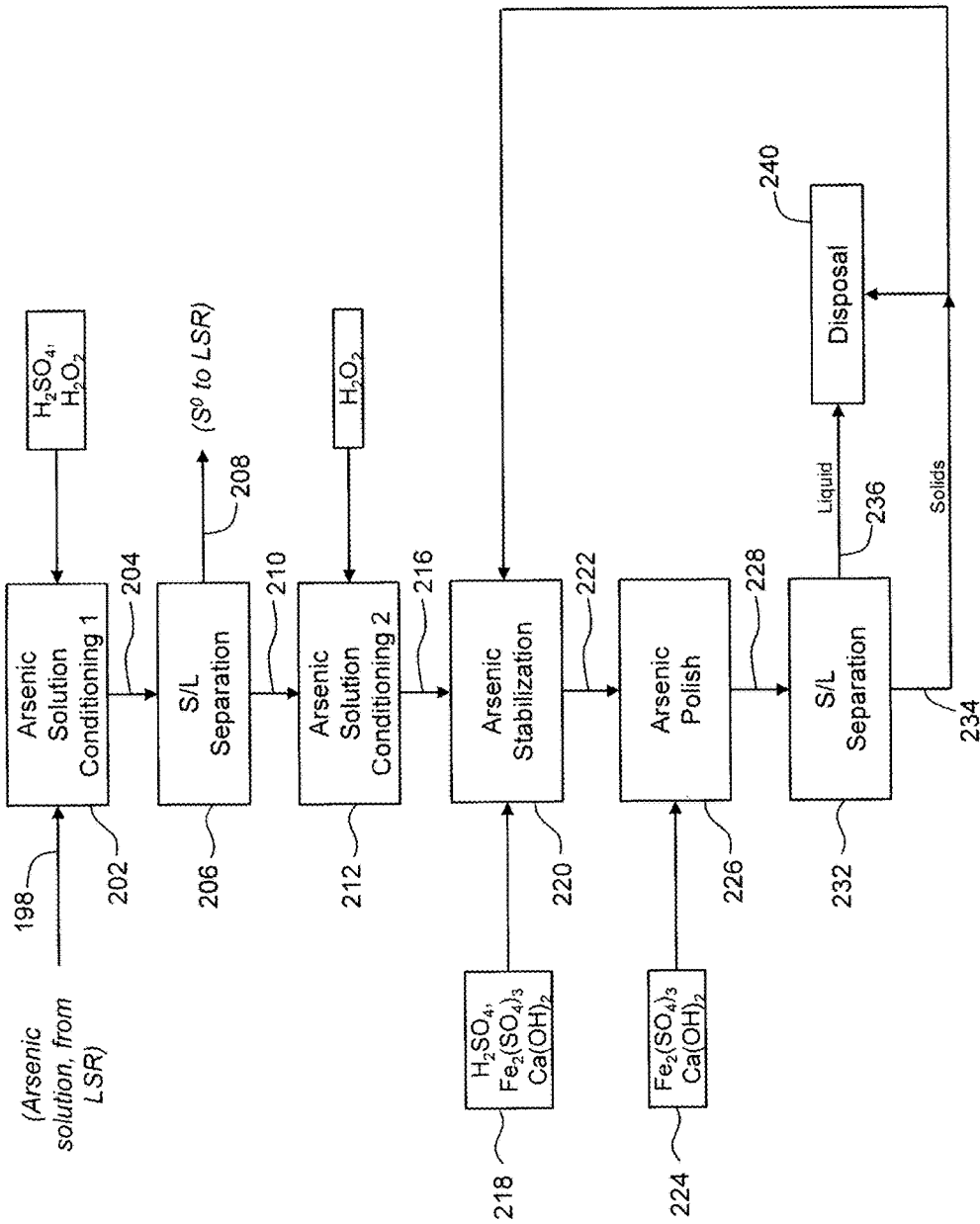


Figure 5

326

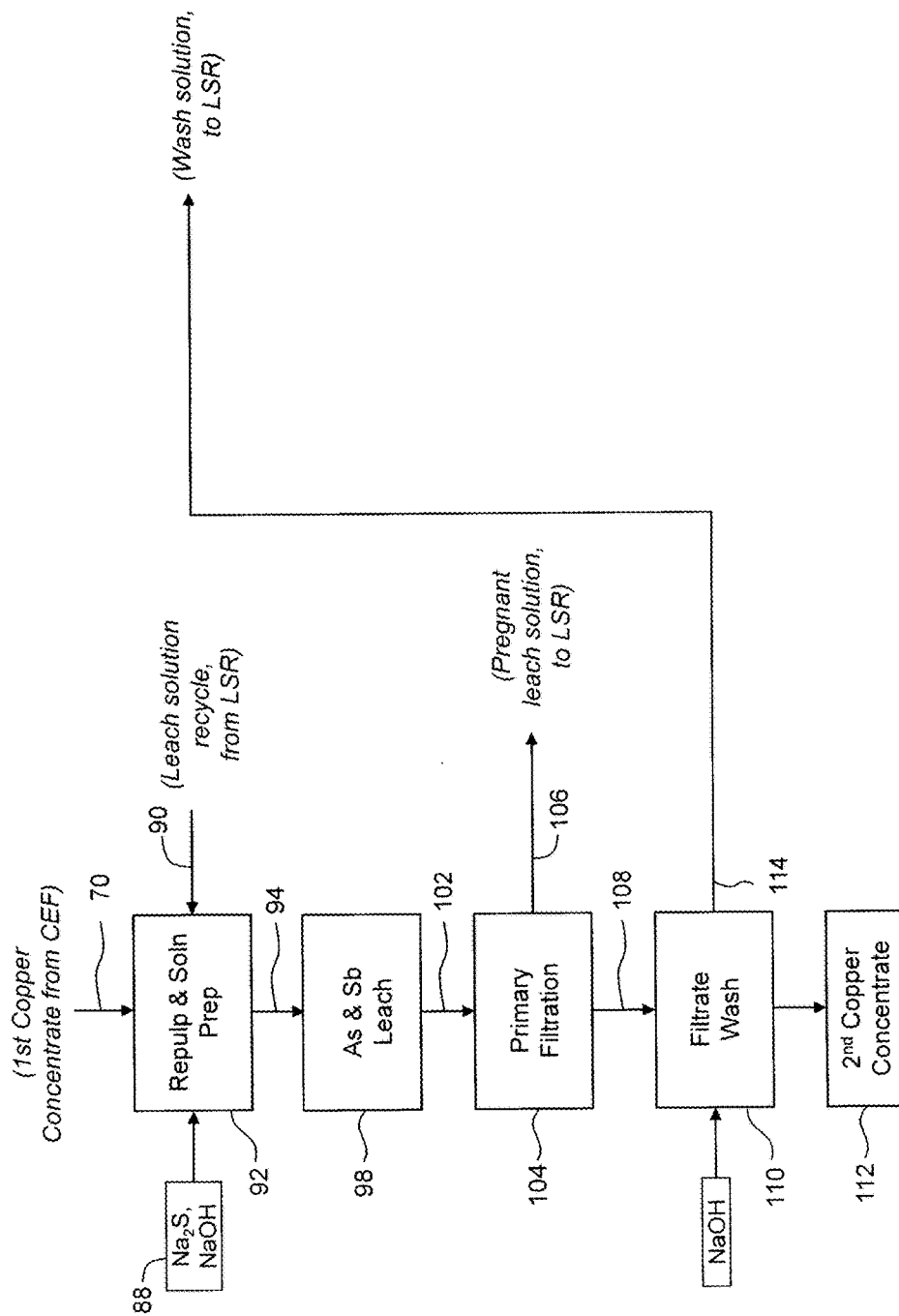


Figure 6

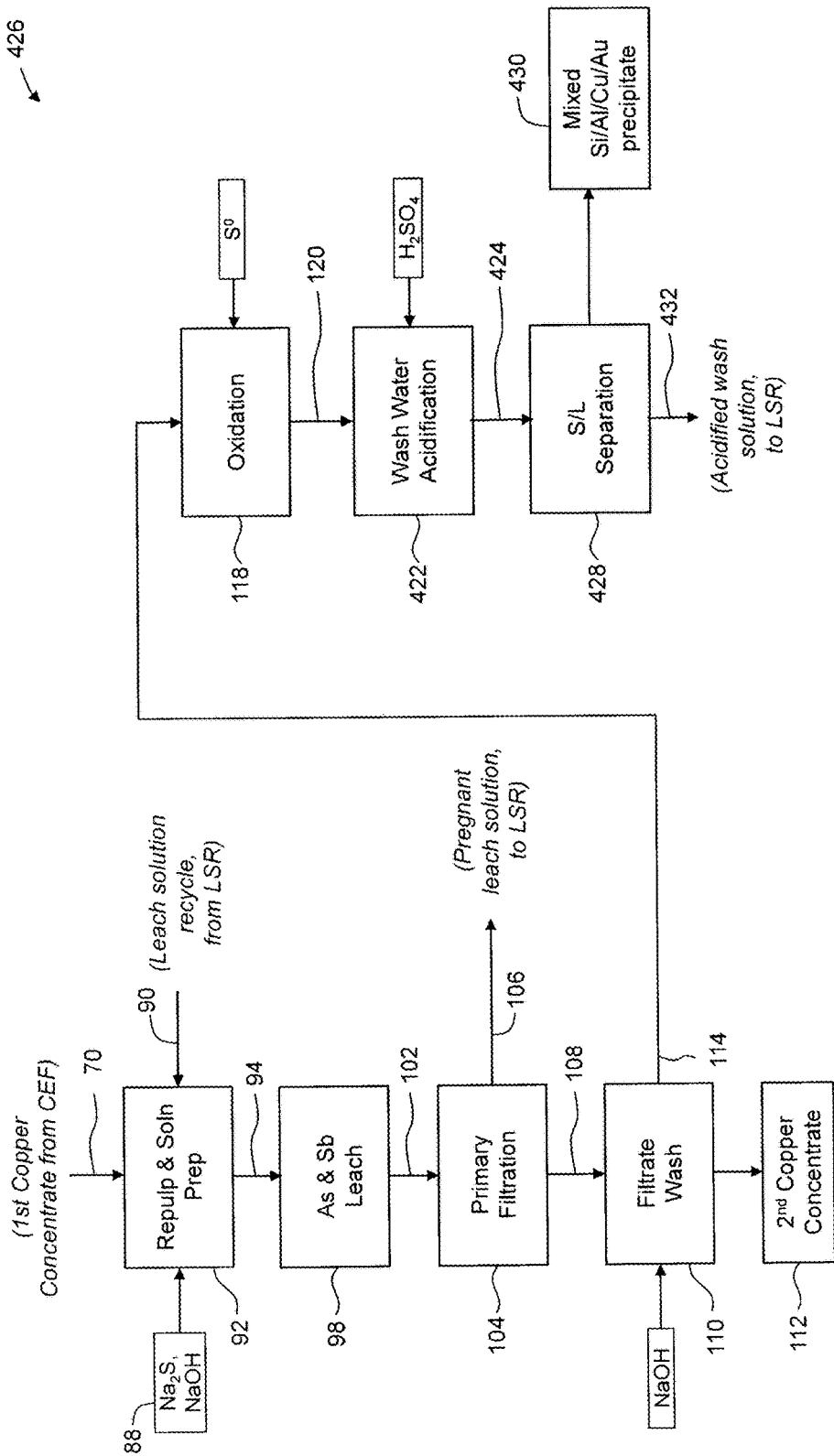


Figure 7



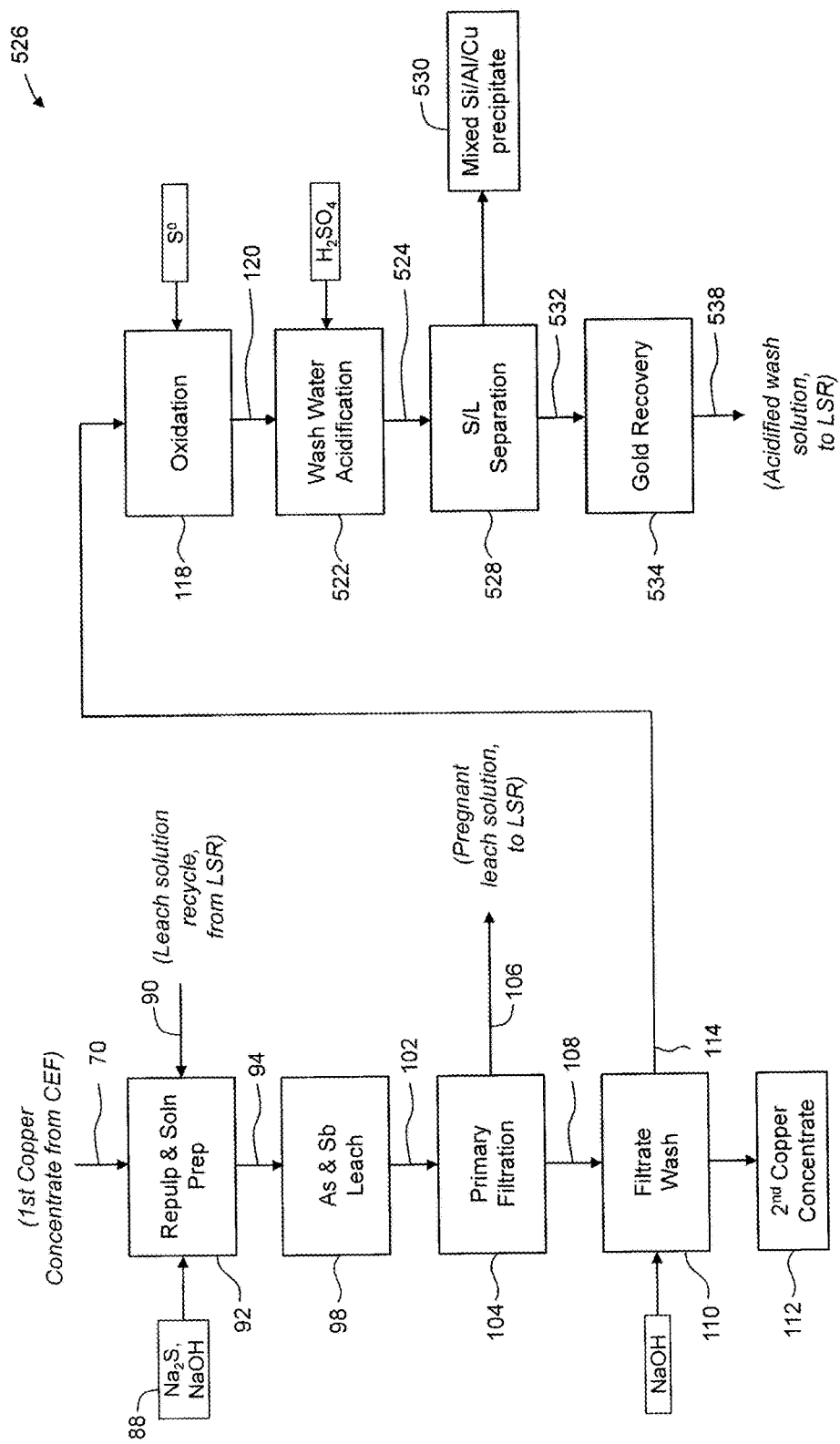


Figure 8

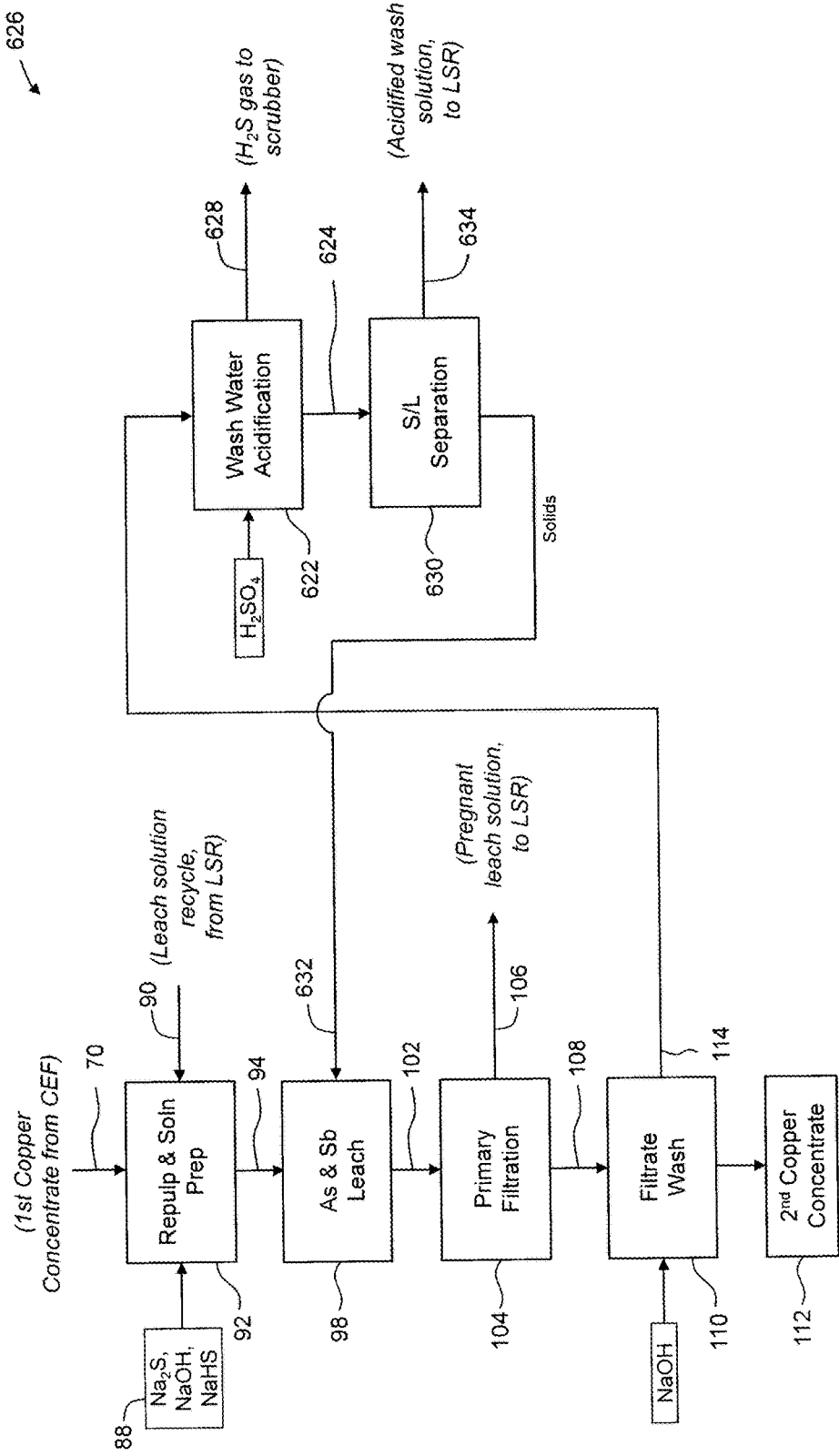


Figure 9

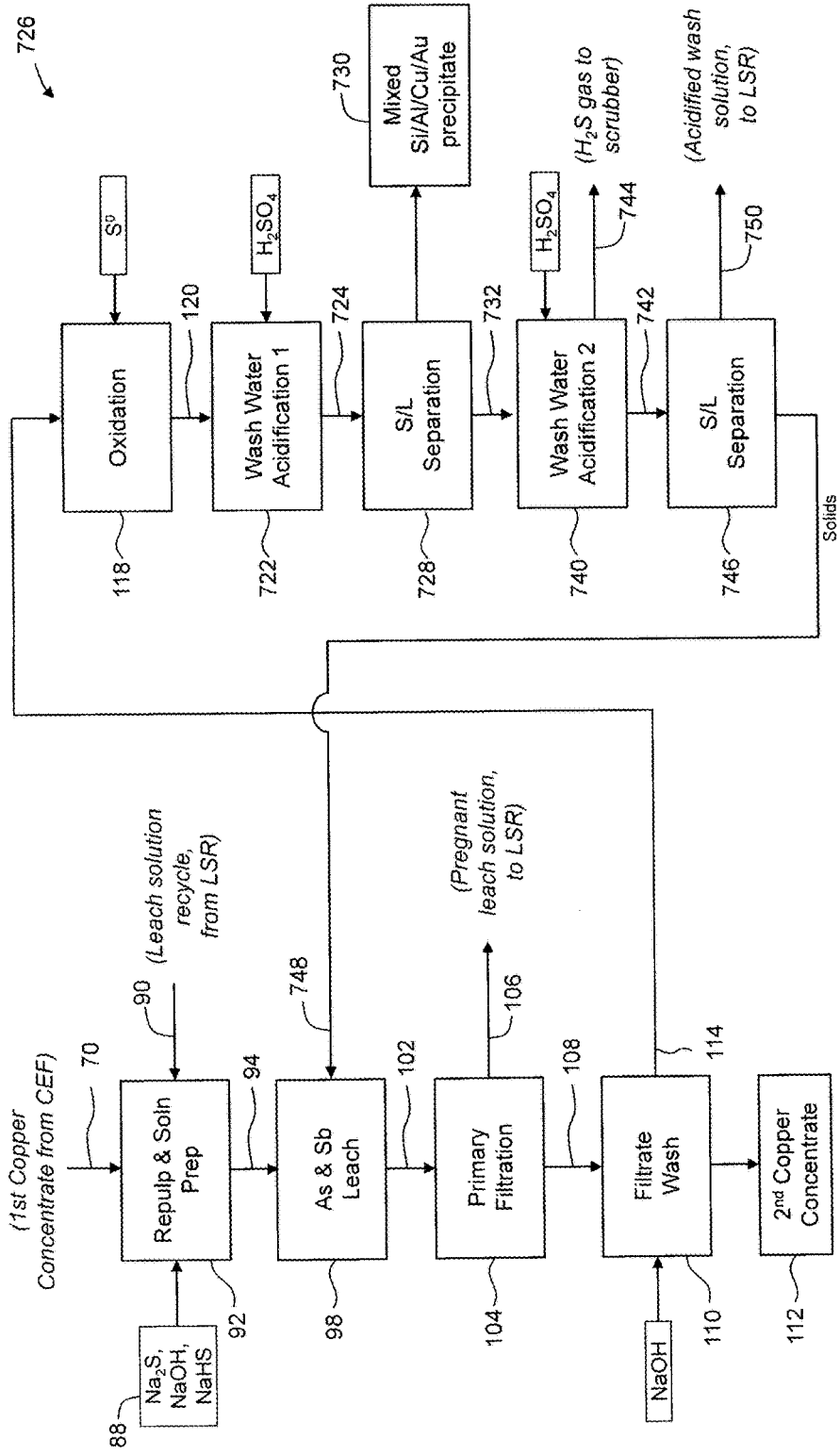


Figure 10

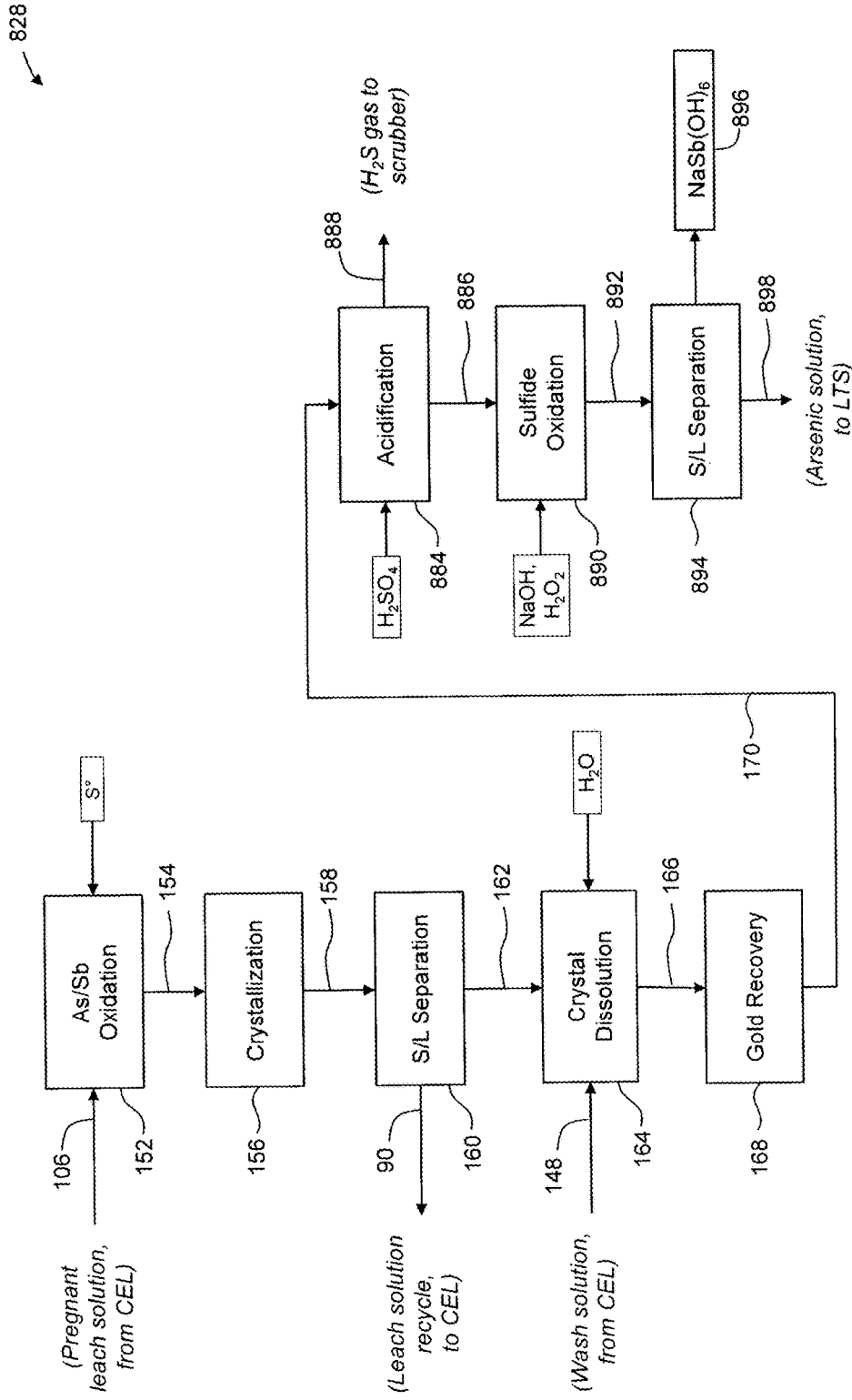


Figure 11

928

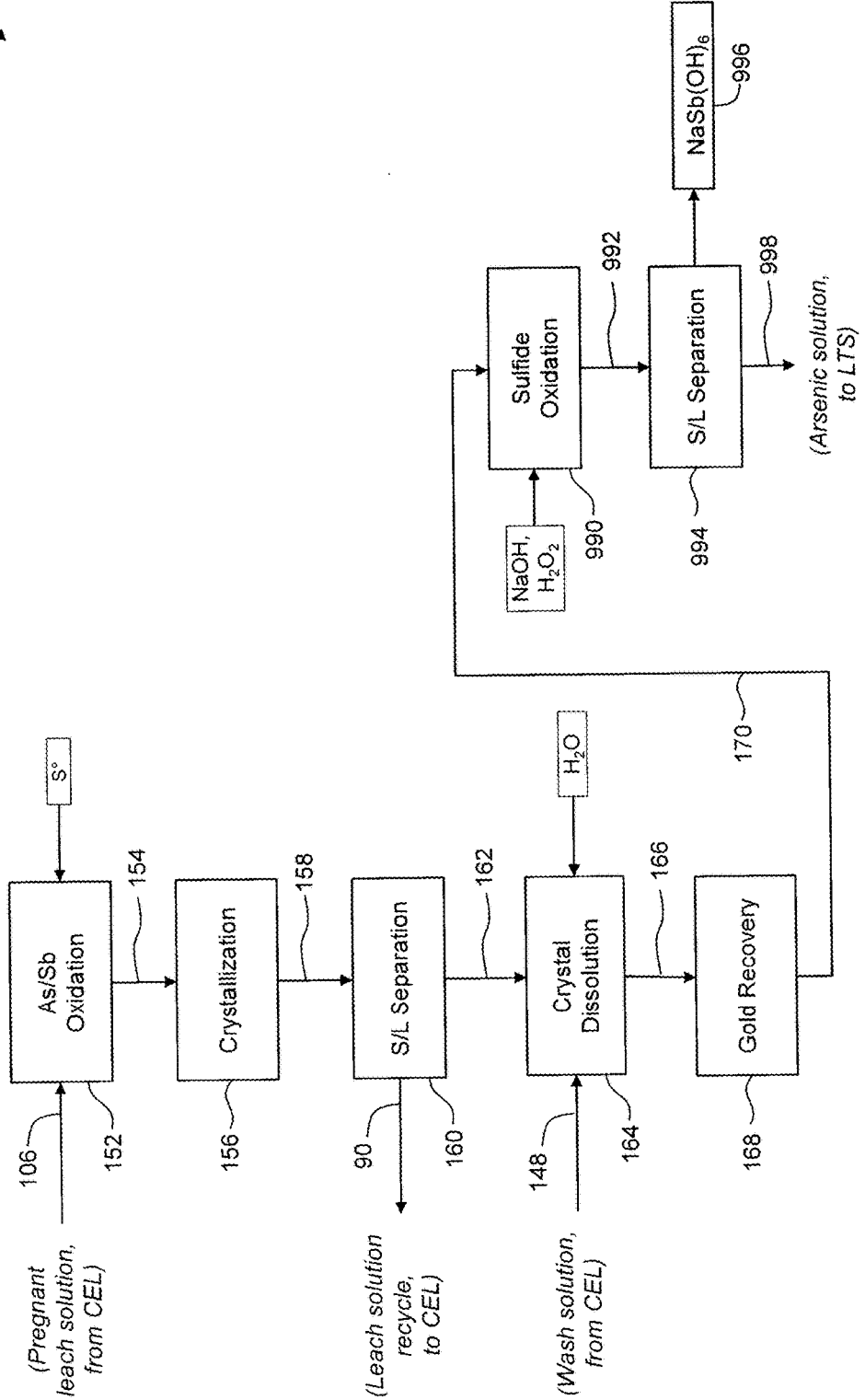


Figure 12

1030

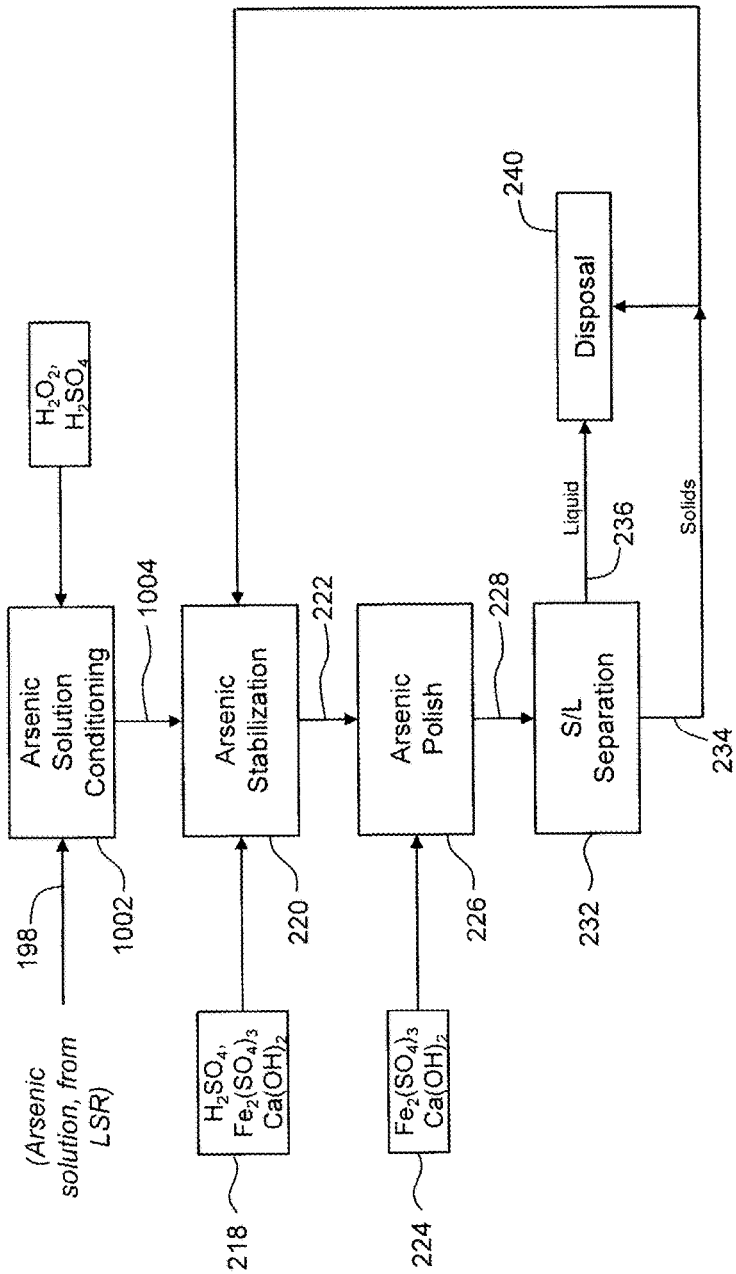


Figure 13

**PROCESS FOR SEPARATION OF AT LEAST ONE METAL SULFIDE FROM A MIXED SULFIDE ORE OR CONCENTRATE**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a divisional application of U.S. patent application Ser. No. 15/850,849, filed on Dec. 21, 2017, which is a divisional application of U.S. patent application Ser. No. 15/115,142, filed on Jul. 28, 2016, which is a national stage application of PCT Patent Application No. PCT/CA2015/000050, filed Jan. 30, 2015, which claims priority to U.S. Provisional Patent Application Ser. No. 61/934,193, filed Jan. 31, 2014, the contents of each of which are hereby incorporated by reference in their entireties.

BACKGROUND OF THE DISCLOSURE

1. Field of the Disclosure

[0002] The subject application relates generally to processing of metal ores or concentrates, and in particular to a process for separation of at least one metal sulfide from such ores or concentrates.

2. Description of the Related Art

[0003] Metallurgical processes are applied to metal ore deposits and such processes can be categorized into three general areas: leaching, solution concentration and purification, and metal recovery.

[0004] Such processes have been previously described. For example, U.S. Pat. No. 3,709,680 to Holmes et al. (1973) is directed to leaching a copper concentrate prepared by flotation using a hot concentrated caustic solution.

[0005] U.S. Pat. No. 3,911,078 to Nadkarni et al. (1975) is directed to a method for removing chemically bonded arsenic and antimony from copper sulfide ores.

[0006] U.S. Pat. No. 4,017,369 to Lindstrom (1977) is directed to the recovery of the antimony, arsenic, mercury and tin from alkaline leach solutions by electrowinning.

[0007] U.S. Pat. No. 4,051,220 to Coltrinari (1977) is directed to a process for treating mixed metal sulfides containing trivalent antimony sulfide. The process involves leaching with sodium sulfide to isolate copper sulfide as an insoluble solid. Following leaching, antimony and arsenic values are oxidized.

[0008] U.S. Pat. No. 5,137,640 to Poncha (1992) is directed to a process for reducing arsenic levels in a solution containing sulfuric acid, water, and arsenic acid by adding copper or a copper-containing compound to the solution to form dissolved copper arsenate, adding alkali solution to precipitate the copper arsenate and to neutralize arsenic and sulfuric acid.

[0009] U.S. Pat. No. 5,290,338 to Anderson et al. (1994) is directed to an antimony recovery process in which an antimony-containing material is leached in a solvent including elemental sulfur and caustic.

[0010] U.S. Pat. No. 5,750,019 to Olper (1998) is directed to a hydrometallurgical and electrochemical process for processing sulfur antimony ores and residues, the end products from which are electrolytic antimony and elemental sulfur.

[0011] Most of the economically significant base metal ore deposits worldwide contain mixed sulfides. Several types of mixed sulfide ores and concentrates may contain relatively large quantities of lead sulfide together with sulfides of other metals, such as copper, antimony and arsenic. Known metallurgical processes do not provide satisfactory metal sulfide separation from such ores and concentrates. It is desirable that certain metal sulfides be separated and recovered from ores and concentrates and converted, if necessary, to a form suitable for commercial sale, while other more deleterious elements (e.g. other metals/metal compounds) may be removed. Deleterious elements are understood to mean elements that are considered commercially deleterious and therefore, can vary widely depending on the commercial application. It is also desirable that the cost of separation of at least one metal sulfide and/or removing deleterious elements from the concentrate at or near the mine be kept low.

[0012] Accordingly, there is a need for an improved process for separation of at least one metal sulfide from a mixed sulfide ore or concentrate.

SUMMARY OF THE DISCLOSURE

[0013] Accordingly, in one aspect there is provided a process for separation of at least one metal sulfide from a mixed sulfide concentrate, the mixed sulfide concentrate having at least one sulfide comprising antimony, arsenic and at least two metals, the at least two metals comprising a first metal and a second metal, the process comprising: subjecting the mixed sulfide concentrate to flotation in which at least one sulfide comprising antimony, arsenic and the first metal is floated and at least one sulfide comprising the second metal is depressed, the flotation yielding a first metal concentrate and a second metal concentrate, the first metal concentrate having the at least one sulfide comprising antimony, arsenic and the first metal, and the second metal concentrate having the at least one sulfide comprising the second metal; leaching the first metal concentrate to yield a further metal concentrate and a leach solution, the further metal concentrate comprising the first metal and the leach solution comprising soluble antimony and soluble arsenic; and one of: (i) oxidizing the leach solution to yield an antimony precipitate and an arsenic solution; (ii) forming a stable arsenic compound from the leach solution; and (iii) oxidizing the leach solution to yield an antimony precipitate and an arsenic solution, and forming a stable arsenic compound from the arsenic solution.

[0014] The leach solution may be oxidized to yield the antimony precipitate and the arsenic solution, and the stable arsenic compound is formed from the arsenic solution. The antimony and arsenic may be present in the mixed sulfide concentrate in a molar ratio of about 0.5:1 to about 1.5:1. The antimony and arsenic may be present in the mixed sulfide concentrate in a molar ratio of about 1:1.

[0015] The mixed sulfide concentrate may comprise the at least two metals, and a major amount of arsenic relative to antimony. The mixed sulfide concentrate may comprise the at least two metals, and a major amount of antimony relative to arsenic.

[0016] The arsenic solution may have an As:Sb concentration ratio of about 10:1 to about 500:1, typically about 20:1 to about 200:1, and more typically about 50:1 to about 100:1.

[0017] The first metal and the second metal may be different metals. The first metal and the second metal may be

the same metal. The first metal and the second metal may be selected from the group consisting of copper, lead, silver, iron, mercury, zinc, and vanadium. The first metal may be copper and the second metal may be lead.

**[0018]** Subjecting the mixed sulfide concentrate to flotation may comprise using one or more of a sulfite salt and a caustic starch solution.

**[0019]** The second metal concentrate may have at least about 50% of the original antimony, the arsenic, and the first metal content of the mixed sulfide concentrate removed. The second metal concentrate may have about 60% to about 90% of the original antimony, arsenic, and the first metal content of the mixed sulfide concentrate removed. The first metal concentrate may have at least about 50% of the original second metal content of the mixed sulfide concentrate removed. The first metal concentrate may have about 65% to about 98% of the original second metal content of the mixed sulfide concentrate removed. The further metal concentrate may have at least about 75% of the original antimony and arsenic content of the mixed sulfide concentrate removed. The further metal concentrate may have about 80% to about 95% of the original antimony and arsenic content of the mixed sulfide concentrate removed.

**[0020]** The process may further comprise: washing solids remaining after the leaching to yield a first wash solution. The process may further comprise: acidifying the first wash solution to form a precipitate and to yield a first wash slurry; and separating the precipitate from the first wash slurry to yield a second wash solution. The process may further comprise: acidifying the second wash solution to precipitate arsenic and antimony species as a slurry; separating the precipitated arsenic and antimony species; and leaching the precipitated arsenic and antimony species with the first metal concentrate during the leaching. The process may further comprise: prior to the acidifying, oxidizing the first wash solution so as to oxidize  $\text{As}^{3+}$  to  $\text{As}^{5+}$  and  $\text{Sb}^{3+}$  to  $\text{Sb}^{5+}$ . The process may further comprise: leaching the precipitate with the first metal concentrate during the leaching.

**[0021]** The oxidizing the leach solution may comprise oxidizing the soluble arsenic and antimony in the leach solution to yield soluble antimony and arsenic thiosalts. The oxidizing the soluble antimony and arsenic in the leach solution may comprise oxidizing with elemental sulfur. The process may further comprise determining an oxidation end point by at least one of wavelength monitoring and oxidation reduction potential (ORP) monitoring. The process may further comprise removing the soluble antimony and arsenic thiosalts from the leach solution by crystallization. The process may further comprise recovering the leach solution for recycling. The removing may comprise cooling the leach solution to induce the crystallization. The cooling may be controlled to avoid crystallization of alkali metal sulfide. The crystallization may comprise forming thioarsenate and thioantimonate salts. The process may further comprise dissolving crystals formed by the crystallization to yield the soluble antimony and arsenic thiosalts. The further metal concentrate may be washed to yield a wash solution, the dissolving comprises dissolving the crystals in the wash solution.

**[0022]** The process may further comprise oxidizing the soluble antimony and arsenic thiosalts to yield the antimony precipitate and the arsenic solution. The oxidizing the soluble antimony and arsenic thiosalts may comprise using an oxidizing agent. The oxidizing agent may be hydrogen

peroxide and/or a metal catalyzed hydroquinone. The oxidizing the soluble antimony and arsenic thiosalts may be carried out at about atmospheric pressure. The process may further comprise: prior to the oxidizing the soluble antimony and arsenic thiosalts, acidifying a solution comprising the soluble antimony and arsenic thiosalts to precipitate arsenic and antimony species as a slurry; and dissolving the precipitated arsenic and antimony species through addition of base to the slurry, wherein the oxidizing comprises oxidizing the dissolved arsenic and antimony species. The process may further comprise: prior to the oxidizing the soluble antimony and arsenic thiosalts, acidifying a solution comprising the soluble antimony and arsenic thiosalts to precipitate an additional antimony sulfide product as a slurry; separating the additional antimony sulfide product from the slurry; acidifying the slurry to precipitate arsenic and antimony species; and dissolving the precipitated arsenic and antimony species through addition of base to the slurry, wherein the oxidizing comprises oxidizing the dissolved arsenic and antimony species. The additional antimony sulfide product may comprise antimony pentasulfide. Hydrogen sulfide gas may be produced, and the hydrogen sulfide gas be passed through a caustic scrubber. A sodium sulfide product or a sodium hydrosulfide product may be formed. The process may further comprise combining the sodium sulfide product or the sodium hydrosulfide product with leach reagents during the leaching.

**[0023]** The antimony precipitate may comprise sodium antimony hydroxide.

**[0024]** The arsenic solution may comprise soluble arsenate.

**[0025]** The forming further comprises returning a portion of the stable arsenic compound to the forming to act as precipitation seed material during the forming.

**[0026]** The process may further comprise, prior to the forming: acidifying the arsenic solution to decompose thio-sulfates, to yield an acidified solution; oxidizing the acidified solution to oxidize residual  $\text{As}^{3+}$  to  $\text{As}^{5+}$  and reduced sulfur species to sulfates, to yield a slurry comprising elemental sulfur; separating elemental sulfur from the slurry to yield a liquid; and oxidizing the liquid to oxidize residual reduced sulfur species, to yield an oxidized solution, wherein the forming comprises forming the stable arsenic compound from the oxidized solution. The process may further comprise using the elemental sulfur as an oxidizing agent for the oxidizing of the leach solution.

**[0027]** The process may further comprise, prior to the forming: oxidizing the arsenic solution to oxidize residual  $\text{As}^{3+}$  to  $\text{As}^{5+}$  and reduced sulfur species to sulfates, to yield an oxidized solution; and acidifying the oxidized solution to yield an acidified oxidized solution, wherein forming comprises forming the stable arsenic compound from the acidified oxidized solution.

**[0028]** The stable arsenic compound may comprise ferric arsenate. The stable arsenic compound may be compliant with toxic characteristic leaching procedure (TCLP) standards.

**[0029]** The at least one sulfide comprising antimony, arsenic and at least two metals may comprise sulfosalts. The sulfosalts may comprise at least one of sulfarsenites, sulfarsenates, sulfantimonites, sulfantimonates and sulfosalts of  $\text{SnS}$  archetype. The sulfosalts may comprise at least one of: tetrahedrite, tennantite, enargite, bournonite, famatinitite, and jamesonite.



**[0030]** The second metal concentrate may be substantially free of antimony, arsenic and the first metal. The further metal concentrate may be substantially free of antimony and arsenic.

**[0031]** In another aspect, there is provided a process for separation of at least one metal sulfide from a mixed sulfide concentrate, the mixed sulfide concentrate having at least one sulfide comprising antimony, arsenic, and at least two metals, the at least two metals comprising a first metal and a second metal, the process comprising: subjecting the mixed sulfide concentrate to flotation using one or more of a sulfite salt and a caustic starch solution in which at least one sulfide comprising antimony, arsenic, and the first metal is floated and at least one sulfide comprising the second metal is depressed, the flotation yielding a first metal concentrate and a second metal concentrate, the first metal concentrate having the at least one sulfide comprising antimony, arsenic, and the first metal, and the second metal concentrate having the at least one sulfide comprising the second metal.

**[0032]** Antimony and arsenic may be present in the mixed sulfide concentrate in a molar ratio of about 0.5:1 to about 1.5:1. Antimony and arsenic may be present in the mixed sulfide concentrate in a molar ratio of about 1:1.

**[0033]** The mixed sulfide concentrate may comprise the at least two metals, and a major amount of arsenic relative to antimony. The mixed sulfide concentrate may comprise the at least two metals, and a major amount of antimony relative to arsenic. The first metal and the second metal may be different metals. The first metal and the second metal may be the same metal. The first metal and the second metal may be selected from the group consisting of copper, lead, silver, iron, mercury, zinc, and vanadium. The first metal may be copper and the second metal may be lead.

**[0034]** The subjecting the mixed sulfide concentrate to flotation further comprises using at least one of a frother and a collector.

**[0035]** The second metal concentrate may have at least about 50% of the original antimony, arsenic, and the first metal content of the mixed sulfide concentrate removed. The second metal concentrate may have about 60% to about 90% of the original antimony, arsenic, and the first metal content of the mixed sulfide concentrate removed. The first metal concentrate may have at least about 50% of the original second metal content of the mixed sulfide concentrate removed. The first metal concentrate may have about 65% to about 98% of the original second metal content of the mixed sulfide concentrate removed. The further metal concentrate may have at least about 75% of the original antimony and arsenic content of the mixed sulfide concentrate removed. The further metal concentrate may have about 80% to about 95% of the original antimony and arsenic content of the mixed sulfide concentrate removed.

**[0036]** The process may further comprise leaching the first metal concentrate to yield a further metal concentrate and a leach solution, the further metal concentrate comprising the first metal and the leach solution comprising soluble arsenic and soluble antimony. The process may further comprise washing solids remaining after the leaching with to yield a first wash solution. The process may further comprise: acidifying the first wash solution to form a precipitate and yield a first wash slurry; and separating the precipitate from the first wash slurry to yield a second wash solution. The process may further comprise: acidifying the second wash

solution to precipitate arsenic and antimony species as a slurry; separating the precipitated arsenic and antimony species; and leaching the precipitated arsenic and antimony species with the first metal concentrate during the leaching. The process may further comprise prior to the acidifying, oxidizing the first wash solution so as to oxidize  $\text{As}^{3+}$  to  $\text{As}^{5+}$  and  $\text{Sb}^{3+}$  to  $\text{Sb}^{5+}$ . The process may further comprise: leaching the precipitate with the first metal concentrate during the leaching.

**[0037]** The sulfides may comprise antimony, arsenic and at least two metals comprise sulfosalts. The sulfosalts may comprise at least one of sulfarsenites, sulfarsenates, sulfantimonites, sulfantimonates and sulfosalts of SnS archetype. The sulfosalts may comprise at least one of tetrahedrite, tennantite, enargite, boumonite, famatinite, and jamesonite.

**[0038]** The second metal concentrate may be substantially free of antimony, arsenic and the first metal. The further metal concentrate may be substantially free of antimony and arsenic.

**[0039]** In another aspect, there is provides a process for leaching a first metal concentrate having at least one sulfide comprising antimony, arsenic, and at least one metal, the process comprising: leaching the first metal concentrate to yield a further metal concentrate and a leach solution, the leach solution comprising soluble arsenic and soluble antimony; removing the soluble antimony and soluble arsenic from the leach solution by crystallization; and recovering the leach solution for recycling.

**[0040]** Antimony and arsenic may be present in the at least one sulfide comprising antimony, arsenic and the at least one metal in a molar ratio of about 0.5:1 to about 1.5:1. Antimony and arsenic may be present in the at least one sulfide comprising antimony, arsenic and the at least one metal in a molar ratio of about 1:1. The mixed sulfide concentrate may comprise the at least one metal, and a major amount of arsenic relative to antimony. The mixed sulfide concentrate may comprise the at least one metal, and a major amount of antimony relative to arsenic.

**[0041]** The at least one sulfide may comprise at least two sulfides comprising different metals. The at least one sulfide may comprise at least two sulfides comprising the same metal.

**[0042]** The at least one metal may be selected from the group consisting of copper, lead, silver, iron, mercury, zinc, and vanadium. The at least one metal may comprise copper. The process may further comprise, prior to the removing: oxidizing the soluble arsenic and antimony in the leach solution to yield soluble antimony and arsenic thiosalts. The oxidizing the soluble antimony and arsenic in the leach solution may comprise oxidizing with elemental sulfur. The process may further comprise determining an oxidation end point by at least one of wavelength monitoring and oxidation reduction potential (ORP) monitoring. The process may further comprise removing the soluble antimony and arsenic thiosalts from the leach solution by crystallization.

**[0043]** The removing may comprise cooling the leach solution to induce the crystallization. The crystallization may comprise forming thioarsenate and thioantimonate salts.

**[0044]** The process may further comprise dissolving crystals formed by the crystallization to yield soluble antimony and arsenic thiosalts. The further metal concentrate may be washed to yield an wash solution, the dissolving comprising dissolving the crystals in the wash solution.

**[0045]** The process may further comprise oxidizing the soluble antimony and arsenic thiosalts to yield an antimony precipitate and an arsenic solution. The oxidizing the soluble antimony and arsenic thiosalts may comprise using an oxidizing agent. The oxidizing agent may be hydrogen peroxide and/or a metal catalyzed hydroquinone. The oxidizing the soluble antimony and arsenic thiosalts may be carried out at about atmospheric pressure. The process may further comprise: prior to the oxidizing the soluble antimony and arsenic thiosalts, acidifying a solution comprising the soluble antimony and arsenic thiosalts to precipitate arsenic and antimony species as a slurry; and dissolving the precipitated arsenic and antimony species through addition of base to the slurry, wherein the oxidizing comprises oxidizing the dissolved arsenic and antimony species. The process may further comprise: prior to the oxidizing the soluble antimony and arsenic thiosalts, acidifying a solution comprising the soluble antimony and arsenic thiosalts to precipitate an additional antimony sulfide product as a slurry; separating the additional antimony sulfide product from the slurry; acidifying the slurry to precipitate arsenic and antimony species; and dissolving the precipitated arsenic and antimony species through addition of base to the slurry, wherein the oxidizing comprises oxidizing the dissolved arsenic and antimony species. The additional antimony sulfide product may comprise antimony pentasulfide. Hydrogen sulfide gas may be produced, and the hydrogen sulfide gas may be passed through a caustic scrubber. A sodium sulfide product or a sodium hydrosulfide product may be formed. The process may further comprise combining the sodium sulfide product or the sodium hydrosulfide product with leach reagents during the leaching. The antimony precipitate may comprise sodium antimony hydroxide.

**[0046]** The arsenic solution may comprise soluble arsenate. The process may further comprise forming a stable arsenic compound from the arsenic solution. The forming further comprises returning a portion of the stable arsenic compound to the forming to act as precipitation seed material during the forming. The process may further comprise, prior to the forming: acidifying the arsenic solution to decompose thiosulfates, to yield an acidified solution; oxidizing the acidified solution to oxidize residual  $\text{As}^{3+}$  to  $\text{As}^{5+}$  and reduced sulfur species to sulfates, to yield a slurry comprising elemental sulfur; separating elemental sulfur from the slurry to yield a liquid; and oxidizing the liquid to oxidize residual reduced sulfur species, to yield an oxidized solution, wherein the forming comprises forming the stable arsenic compound from the oxidized solution. The process may further comprise using the elemental sulfur for use as an oxidizing agent for the oxidizing of the leach solution. The process may further comprise, prior to the forming: oxidizing the arsenic solution to oxidize residual  $\text{As}^{3+}$  to  $\text{As}^{5+}$  and reduced sulfur species to sulfates, to yield an oxidized solution; and acidifying the oxidized solution to yield an acidified oxidized solution, wherein forming comprises forming the stable arsenic compound from the acidified oxidized solution. The stable arsenic compound may comprise ferric arsenate. The stable arsenic compound may be compliant with toxic characteristic leaching procedure (TCLP) standards.

**[0047]** The at least one sulfide comprising antimony, arsenic and the at least one metal may comprise one or more sulfosalts. The one or more sulfosalts may comprise at least

one of sulfarsenites, sulfarsenates, sulfantimonites, sulfantimonates and sulfosalts of SnS archetype. The one or more sulfosalts may comprise at least one of tetrahedrite, tennantite, enargite, boumronite, famatinite, and jamesonite.

**[0048]** The further metal concentrate may be substantially free of antimony and arsenic.

**[0049]** In another aspect, there is provided a process for separation of antimony and arsenic from a leach solution comprising soluble antimony and arsenic, the process comprising: oxidizing the soluble antimony and arsenic in the leach solution so as to reach an oxidation end point determined by at least one of wavelength monitoring and oxidation reduction potential (ORP) monitoring, to yield soluble antimony and arsenic thiosalts; and oxidizing the soluble antimony and arsenic thiosalts to yield an antimony precipitate and an arsenic solution.

**[0050]** Antimony and arsenic may be in the leach solution in a molar ratio of about 0.5:1 to about 1.5:1. Antimony and arsenic may be present in the leach solution in a molar ratio of about 1:1. The leach solution may comprise a major amount of arsenic relative to antimony. The leach solution may comprise a major amount of antimony relative to arsenic.

**[0051]** The oxidizing the soluble antimony and arsenic in the leach solution may comprise oxidizing with elemental sulfur.

**[0052]** The process may further comprise removing the soluble antimony and arsenic thiosalts from the leach solution by crystallization. The process may further comprise recovering the leach solution for recycling. The removing may comprise cooling the leach solution to induce the crystallization. The cooling may be controlled to avoid crystallization of alkali metal sulfide. The crystallization may comprise forming thioarsenate and thioantimonate salts. The process may further comprise dissolving crystals formed by the crystallization to yield the soluble antimony and arsenic thiosalts.

**[0053]** The oxidizing the soluble antimony and arsenic thiosalts may comprise using an oxidizing agent. The oxidizing agent may be hydrogen peroxide and/or a metal catalyzed hydroquinone.

**[0054]** The oxidizing the soluble antimony and arsenic thiosalts may be carried out at about atmospheric pressure.

**[0055]** The process may further comprise: prior to the oxidizing the soluble antimony and arsenic thiosalts, acidifying a solution comprising the soluble antimony and arsenic thiosalts to precipitate arsenic and antimony species as a slurry; and dissolving the precipitated arsenic and antimony species through addition of base to the slurry, wherein the oxidizing comprises oxidizing the dissolved arsenic and antimony species.

**[0056]** The process may further comprise: prior to the oxidizing the soluble antimony and arsenic thiosalts, acidifying a solution comprising the soluble antimony and arsenic thiosalts to precipitate an additional antimony sulfide product as a slurry; separating the additional antimony sulfide product from the slurry; acidifying the slurry to precipitate arsenic and antimony species; and dissolving the precipitated arsenic and antimony species through addition of base to the slurry, wherein the oxidizing comprises oxidizing the dissolved arsenic and antimony species. The additional antimony sulfide product comprises antimony pentasulfide. Hydrogen sulfide gas may be produced and the

hydrogen sulfide gas may be passed through a caustic scrubber. A sodium sulfide product or a sodium hydrosulfide product may be formed.

**[0057]** The antimony precipitate may comprise sodium antimony hydroxide.

**[0058]** The arsenic solution may comprise soluble arsenate.

**[0059]** The process may further comprise forming a stable arsenic compound from the arsenic solution. The forming further comprises returning a portion of the stable arsenic compound to the forming to act as precipitation seed material during the forming. The process may further comprise, prior to the forming: acidifying the arsenic solution to decompose thiosulfates, to yield an acidified solution; oxidizing the acidified solution to oxidize residual  $As^{3+}$  to  $As^{5+}$  and reduced sulfur species to sulfates, to yield a slurry comprising elemental sulfur; separating elemental sulfur from the slurry to yield a liquid; and oxidizing the liquid to oxidize residual reduced sulfur species, to yield an oxidized solution, wherein the forming comprises forming the stable arsenic compound from the oxidized solution. The process may further comprise using the elemental sulfur for use as an oxidizing agent for the oxidizing of the leach solution. The process may further comprise, prior to the forming: oxidizing the arsenic solution to oxidize residual  $As^{3+}$  to  $As^{5+}$  and reduced sulfur species to sulfates, to yield an oxidized solution; and acidifying the oxidized solution to yield an acidified oxidized solution, wherein forming comprises forming the stable arsenic compound from the acidified oxidized solution. The stable arsenic compound may comprise ferric arsenate. The stable arsenic compound may be compliant with toxic characteristic leaching procedure (TCLP) standards.

**[0060]** In another aspect, there is provided a stabilization process for an arsenic solution derived from a mixed sulfide concentrate, the mixed sulfide concentrate having at least one sulfide comprising antimony, arsenic and at least one metal, the process comprising: forming a stable arsenic compound from the arsenic solution, at about atmospheric pressure.

**[0061]** Antimony and arsenic may be present in the mixed sulfide concentrate in a molar ratio of about 0.5:1 to about 1.5:1. Antimony and arsenic may be present in the mixed sulfide concentrate in a molar ratio of about 1:1.

**[0062]** The mixed sulfide concentrate may comprise the at least one metal, and a major amount of arsenic relative to antimony. The mixed sulfide concentrate may comprise the at least one metal, and a major amount of antimony relative to arsenic.

**[0063]** The arsenic solution may have an As:Sb concentration (g/L) ratio of about 10:1 to about 500:1, typically about 20:1 to about 200:1, and more typically about 50:1 to about 100:1.

**[0064]** The at least one metal may be selected from the group consisting of copper, lead, silver, iron, mercury, zinc, and vanadium. The at least one metal may comprise copper.

**[0065]** The arsenic solution may comprise soluble arsenate.

**[0066]** The process may further comprise forming a stable arsenic compound from the arsenic solution for disposal. The forming further comprises returning a portion of the stable arsenic compound to the forming to act as precipitation seed material during the forming. The process may further comprise, prior to the forming: acidifying the arsenic

solution to decompose thiosulfates, to yield an acidified solution; oxidizing the acidified solution to oxidize residual  $As^{3+}$  to  $As^{5+}$  and reduced sulfur species to sulfates, to yield a slurry comprising elemental sulfur; separating elemental sulfur from the slurry to yield a liquid; and oxidizing the liquid to oxidize residual reduced sulfur species, to yield an oxidized solution, wherein the forming comprises forming the stable arsenic compound from the oxidized solution. The process may further comprise using the elemental sulfur for use as an oxidizing agent for the oxidizing of the leach solution. The process may further comprise, prior to the forming: oxidizing the arsenic solution to oxidize residual  $As^{3+}$  to  $As^{5+}$  and reduced sulfur species to sulfates, to yield an oxidized solution; and acidifying the oxidized solution to yield an acidified oxidized solution, wherein forming comprises forming the stable arsenic compound from the acidified oxidized solution. The stable arsenic compound may comprise ferric arsenate. The stable arsenic compound may be compliant with toxic characteristic leaching procedure (TCLP) standards.

**[0067]** In another aspect, there is provided a stabilization process for an arsenic solution comprising thiosulfates, the process comprising: acidifying the arsenic solution to decompose the thiosulfates, to yield an acidified solution; oxidizing the acidified solution to oxidize residual  $As^{3+}$  to  $As^{5+}$  and reduced sulfur species to sulfates, to yield a slurry comprising elemental sulfur; separating elemental sulfur from the slurry to yield a liquid; oxidizing the liquid to oxidize residual reduced sulfur species, to yield an oxidized solution; and forming a stable arsenic compound from the oxidized solution.

**[0068]** The process may further comprise forming a stable arsenic compound from the oxidized solution, at about atmospheric pressure. The stable arsenic compound may comprise ferric arsenate. The stable arsenic compound may be compliant with toxic characteristic leaching procedure (TCLP) standards.

**[0069]** The arsenic solution may be derived from a mixed sulfide concentrate, the mixed sulfide concentrate having at least one sulfide comprising antimony, arsenic and at least one metal. Antimony and arsenic may be present in the mixed sulfide concentrate in a molar ratio of about 0.5:1 to about 1.5:1. Antimony and arsenic may be present in the mixed sulfide concentrate in a molar ratio of about 1:1. The mixed sulfide concentrate may comprise the at least one metal, and a major amount of arsenic relative to antimony. The mixed sulfide concentrate may comprise the at least one metal, and a major amount of antimony relative to arsenic. The at least one metal may be selected from the group consisting of copper, lead, silver, iron, mercury, zinc, and vanadium.

**[0070]** In still another aspect, there is provided a stabilization process for an arsenic solution, the process comprising: oxidizing the arsenic solution to oxidize  $As^{3+}$  to  $As^{5+}$  and reduced sulfur species to sulfates, to yield an oxidized solution; and acidifying the oxidized solution to yield an acidified oxidized solution; and forming a stable arsenic compound from the acidified oxidized solution.

**[0071]** The process may further comprise forming the stable arsenic compound from the oxidized solution at about atmospheric pressure. The stable arsenic compound may comprise ferric arsenate. The stable arsenic compound may be compliant with toxic characteristic leaching procedure (TCLP) standards.

**[0072]** The arsenic solution may be derived from a mixed sulfide concentrate, the mixed sulfide concentrate having at least one sulfide comprising antimony, arsenic and at least one metal. Antimony and arsenic may be present in the mixed sulfide concentrate in a molar ratio of about 0.5:1 to about 1.5:1. Antimony and arsenic may be present in the mixed sulfide concentrate in a molar ratio of about 1:1. The mixed sulfide concentrate may comprise the at least one metal, and a major amount of arsenic relative to antimony. The mixed sulfide concentrate may comprise the at least one metal, and a major amount of antimony relative to arsenic. The at least one metal may be selected from the group consisting of copper, lead, silver, iron, mercury, zinc, and vanadium.

**[0073]** In accordance with the above aspects, the sodium concentration of the oxidized solution may be at least about 10 g/L. The sodium concentration of the oxidized solution may be about 30 g/L to about 70 g/L. The sodium concentration of the oxidized solution may be about 50 g/L to about 60 g/L.

**[0074]** In accordance with the above aspects, the process may further comprise extracting at least one precious metal. The extracting may comprise utilizing at least one of an ion exchange resin and a precipitation process. The precious metal may be gold.

**[0075]** In accordance with the above aspects, the wavelength monitoring may be colorimetry.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0076]** Embodiments will now be described more fully with reference to the accompanying drawings in which:

**[0077]** FIG. 1 is a flowchart showing an embodiment of a process for separation of metal sulfides from a mixed sulfide concentrate;

**[0078]** FIG. 2 is a flowchart showing an embodiment of a concentrate enrichment flotation process forming part of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1;

**[0079]** FIG. 3 is a flowchart showing an embodiment of a concentrate enrichment leach process forming part of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1;

**[0080]** FIG. 4 is a flowchart showing an embodiment of a leach solution recovery process forming part of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1;

**[0081]** FIG. 5 is a flowchart showing an embodiment of a leach tails stabilization process forming part of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1;

**[0082]** FIG. 6 is a flowchart showing another embodiment of a concentrate enrichment leach process forming part of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1;

**[0083]** FIG. 7 is a flowchart showing still another embodiment of a concentrate enrichment leach process forming part of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1;

**[0084]** FIG. 8 is a flowchart showing still another embodiment of a concentrate enrichment leach process forming part of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1;

**[0085]** FIG. 9 is a flowchart showing still another embodiment of a concentrate enrichment leach process forming part

of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1;

**[0086]** FIG. 10 is a flowchart showing still yet another embodiment of a concentrate enrichment leach process forming part of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1;

**[0087]** FIG. 11 is a flowchart showing another embodiment of a leach solution recovery process forming part of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1;

**[0088]** FIG. 12 is a flowchart showing still another embodiment of a leach solution recovery process forming part of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1; and

**[0089]** FIG. 13 is a flowchart showing another embodiment of a leach tails stabilization process forming part of the process for separation of metal sulfides from a mixed sulfide concentrate of FIG. 1.

#### DETAILED DESCRIPTION OF THE DISCLOSURE

**[0090]** In embodiments, a process is provided for separation of at least one metal sulfide from a mixed sulfide ore or concentrate.

**[0091]** The mixed sulfide concentrate comprises at least one sulfide having at least one metal and/or at least one semi-metal. It is understood, when used herein, that at least one sulfide having at least one metal and/or at least one semi-metal may be selected from, for example, any sulfur-bearing compound of one or more metals; any sulfur-bearing compound of one or more semi-metals; any sulfur-bearing compound of one or more metals and one or more semi-metals, such as, and without being limited thereto, sulfosalts; and mixtures thereof. The one or more metals may be selected from, for example, copper, lead, silver, iron, mercury, zinc, or vanadium. The one or more semi-metals may be selected from, for example, arsenic, antimony, bismuth or germanium. As will be understood, sulfosalts comprise one or more metals, one or more semi-metals, and sulfur. Sulfosalts containing arsenic include sulfarsenites, such as tennantite, and sulfarsenates, such as enargite. Sulfosalts containing antimony include sulfantimonites, such as tetrahedrite and boumnonite, sulfantimonates, such as famatinite, and sulfosalts of SnS archetype, such as jamesonite. It is known to be difficult to recover certain metals from such minerals. It is desirable to be able to recover, for example, metals, such as copper, from concentrates containing metal arsenic sulfosalts minerals and metal antimony sulfosalts minerals using an economically viable, hydrometallurgical process, while converting deleterious elements into one or more environmentally stable products.

**[0092]** In another embodiment, there is provided a process for separation of at least one metal sulfide from a mixed sulfide concentrate, where the mixed sulfide concentrate has at least one sulfide comprising antimony, arsenic and at least two metals, and the at least two metals comprise a first metal and a second metal. The process comprises: subjecting the mixed sulfide concentrate to flotation in which at least one sulfide comprising antimony, arsenic and the first metal is floated and at least one sulfide comprising the second metal is depressed, the flotation yielding a first metal concentrate and a second metal concentrate, the first metal concentrate having the at least one sulfide comprising antimony, arsenic and the first metal, and the second metal concentrate having

the at least one sulfide comprising the second metal; leaching the first metal concentrate to yield a further metal concentrate and a leach solution, the further metal concentrate comprising the first metal and the leach solution comprising soluble antimony and soluble arsenic; and one of: (i) oxidizing the leach solution to yield an antimony precipitate and an arsenic solution; (ii) forming a stable arsenic compound from the leach solution; and (iii) oxidizing the leach solution to yield an antimony precipitate and an arsenic solution, and forming a stable arsenic compound from the arsenic solution.

**[0093]** In an embodiment of the process, the mixed sulfide concentrate is subjected to flotation in which copper, antimony, and arsenic sulfides are floated and lead sulfide is depressed. The flotation yields a lead concentrate comprising the lead sulfide and a first copper concentrate comprising the copper, antimony, and arsenic sulfides. The first copper concentrate is then leached to yield a second copper concentrate comprising the copper sulfide, and a leach solution comprising soluble arsenic and antimony. The leach solution is oxidized to yield an antimony precipitate and an arsenic solution. In other embodiments, a stable arsenic compound is formed from the arsenic solution for disposal. In additional embodiments, the lead concentrate is, substantially free of the copper, arsenic and antimony sulfides and/or the second copper concentrate is substantially free of the arsenic and antimony.

**[0094]** In still other embodiments, a specific flotation process is provided. A mixed sulfide concentrate comprising lead, copper, antimony and arsenic sulfide is subjected to flotation. The process comprises subjecting the mixed sulfide concentrate to flotation using one or more of a sulfite salt and a caustic starch solution in which lead sulfide (e.g. galena) is depressed in comparison to the copper, antimony and arsenic sulfides. The flotation provides a lead concentrate separate from a first copper concentrate. The lead concentrate comprises the lead sulfide and the first copper concentrate comprises the copper, arsenic and antimony sulfides (e.g. copper sulfosalts). In additional embodiments, the lead concentrate is substantially free of the copper, arsenic and antimony sulfides.

**[0095]** In another embodiment, there is provided a process for separation of at least one metal sulfide from a mixed sulfide concentrate, the mixed sulfide concentrate having at least one sulfide comprising antimony, arsenic, and at least two metals, the at least two metals comprising a first metal and a second metal. The process comprises: subjecting the mixed sulfide concentrate to flotation using one or more of a sulfite salt and a caustic starch solution in which at least one sulfide comprising antimony, arsenic, and the first metal is floated and at least one sulfide comprising the second metal is depressed, the flotation yielding a first metal concentrate and a second metal concentrate, the first metal concentrate having the at least one sulfide comprising antimony, arsenic, and the first metal, and the second metal concentrate having the at least one sulfide comprising the second metal.

**[0096]** In still other embodiments, a process for leaching a first copper concentrate comprising copper, antimony and arsenic sulfides (e.g. copper sulfosalts) is provided. The first copper concentrate is leached in an alkaline environment to yield a second copper concentrate, and a first leach solution comprising soluble arsenic and antimony. The soluble antimony and arsenic are removed from the leach solution by

crystallization. The leach solution is recovered for recycling. In other embodiments, the second copper concentrate is substantially free of the arsenic and antimony sulfides.

**[0097]** In another embodiment, there is provided a process for leaching a first metal concentrate having at least one sulfide comprising antimony, arsenic, and at least one metal. The process comprises: leaching the first metal concentrate to yield a further metal concentrate and a leach solution, the further metal concentrate comprising the first metal and the leach solution comprising soluble arsenic and soluble antimony; removing the soluble antimony and soluble arsenic from the leach solution by crystallization; and recovering the leach solution for recycling.

**[0098]** In still other embodiments, a process for separation of antimony and arsenic from a leach solution comprising soluble antimony and arsenic is provided. The soluble antimony and arsenic in the leach solution are oxidized to reach an oxidation endpoint determined by at least one of wavelength monitoring and oxidation reduction potential (ORP) monitoring, to yield soluble antimony and arsenic thiosalts. The soluble antimony and arsenic thiosalts are oxidized to yield an antimony precipitate and an arsenic solution.

**[0099]** In another embodiment, there is provided a process for separation of antimony and arsenic from a leach solution comprising soluble antimony and arsenic, the process comprising: oxidizing the soluble antimony and arsenic in the leach solution so as to reach an oxidation end point determined by at least one of wavelength monitoring and oxidation reduction potential (ORP) monitoring, to yield soluble antimony and arsenic thiosalts; and oxidizing the soluble antimony and arsenic thiosalts to yield an antimony precipitate and an arsenic solution.

**[0100]** In further embodiments, a stabilization process for an arsenic solution derived from a mixed sulfide concentrate is provided, where the mixed sulfide concentrate comprises lead, copper, antimony and arsenic sulfides. The process comprises forming a stable arsenic compound from the arsenic solution, at about atmospheric pressure (e.g. about standard atmospheric pressure), optionally, for disposal. Therefore, the stabilization process does not take place in an autoclave.

**[0101]** In another embodiment, there is provided a stabilization process for an arsenic solution derived from a mixed sulfide concentrate, the mixed sulfide concentrate having at least one sulfide comprising antimony, arsenic and at least one metal. The process comprises: forming a stable arsenic compound from the arsenic solution, at about atmospheric pressure.

**[0102]** In another embodiment, there is provided a stabilization process for an arsenic solution comprising thiosulfates. The process comprises: acidifying the arsenic solution to decompose the thiosulfates, to yield an acidified solution; oxidizing the acidified solution to oxidize residual  $\text{As}^{3+}$  to  $\text{As}^{5+}$  and reduced sulfur species to sulfates, to yield a slurry comprising elemental sulfur; separating elemental sulfur from the slurry to yield a liquid; oxidizing the liquid to oxidize residual reduced sulfur species, to yield an oxidized solution; and forming a stable arsenic compound from the oxidized solution.

**[0103]** In another embodiment, there is provided a stabilization process for an arsenic solution. The process comprises: oxidizing the arsenic solution to oxidize  $\text{As}^{3+}$  to  $\text{As}^{5+}$  and reduced sulfur species to sulfates, to yield an oxidized

solution; and acidifying the oxidized solution to yield an acidified oxidized solution; and forming a stable arsenic compound from the acidified oxidized solution.

[0104] It is understood that, when used herein, that an autoclave is a pressurized vessel used for chemical reactions and other processes.

[0105] Turning now to FIG. 1, an embodiment for a process for separation of metal sulfides from a mixed-sulfide concentrate comprising sulfosalts is shown, and is generally indicated by reference numeral 20.

[0106] Process 20 comprises a plurality of sub-processes that are carried out generally in sequence to process a mixed-sulfide concentrate 22 for separating and recovering metal sulfides therefrom. The mixed-sulfide concentrate 22 is formed from ore using one or more processes known to those skilled in the art, and comprises lead, copper, antimony and arsenic sulfides, as well as other minerals and precious metals. More specifically, the mixed-sulfide concentrate 22 is lead-rich and predominantly comprises galena (PbS) and copper sulfosalts, with antimony and arsenic being present in the mixed-sulfide concentrate 22 in any molar ratio. Typically, the antimony and arsenic are present in the mixed-sulfide concentrate 22 in a molar ratio of about 0.5:1 to about 1.5:1, and more typically in a molar ratio of about 1:1. In the embodiment shown, the sub-processes include a concentrate enrichment flotation process 24, a concentrate enrichment leaching process 26, a leach solution recovery process 28, and a leach tails stabilization process 30.

[0107] Certain embodiments of the sub-processes are outlined below with respect to FIGS. 2 to 13.

[0108] FIG. 2 shows steps of the concentrate enrichment flotation process 24. In the process 24, copper and lead are generally separated by a series of flotation steps in which copper minerals are floated and lead sulfide is depressed. Process 24 begins with the mixed-sulfide concentrate 22 being delivered to a primary conditioner 36, where conditioning reagents, described below, are added to the concentrate to form a primary conditioner pulp 38 having a solids content of about 8% by weight to about 15% by weight, and having a pH of about 5.5 to about 7.0. The primary conditioner pulp 38 is then transferred to a rougher 40 where it undergoes flotation. The rougher 40 yields a lead-deficient rougher concentrate 42, which is collected and transferred to a cleaning conditioner 44. The rougher 40 also yields lead-rich rougher tailings 46, which are transferred to a scavenger conditioner 48 where conditioning reagents are combined therewith to form a rougher tailings pulp 50. The rougher tailings pulp 50 is then fed to a rougher scavenger 52, where it undergoes further flotation. The rougher scavenger 52 yields a lead-deficient scavenger concentrate 54, which is collected and transferred to the cleaning conditioner 44. The rougher scavenger 52 also yields lead-rich scavenger tailings 56, which are subjected to solid-liquid separation 58 to remove liquid so as to yield a solid, clean lead concentrate. In this embodiment, the clean lead concentrate 60 predominantly contains galena (PbS). The lead concentrate 60 is substantially free of copper, antimony and arsenic sulfides. Typically, at least about 50% of the original copper, antimony and arsenic sulfide content of the mixed sulfide concentrate 22 has been removed; more typically, about 50% to about 95%, about 60% to about 90%, or about 65% to about 85% has been removed.

[0109] In the cleaning conditioner 44, conditioning reagents are combined with the lead-deficient concentrates

42, 54 and 76 to form a secondary conditioner pulp 62 having a solids content of about 10% to about 20%, and having a pH of about 5.5 to about 7.5. The secondary conditioner pulp 62 is subjected to a cleaning process 64, where it undergoes further flotation. The cleaning process 64 may comprise a single cleaning flotation bank, or may comprise two or more cleaning flotation banks (not shown) connected in series, such that concentrate from each upstream bank is collected and transferred to the next bank downstream in the series, and tailings from each downstream bank are fed to the previous bank upstream in the series. As is known in the art, each flotation bank includes one or more flotation cells connected in series. Concentrate 66 from the cleaning process 64 is collected and subjected to solid-liquid separation 68 so as to yield a solid, first copper concentrate 70 (e.g. a "dirty" copper concentrate). The first copper concentrate 70 is substantially free of lead sulfide(s). Typically, at least about 50% of the original lead sulfide content of the mixed sulfide concentrate 22 has been removed, more typically, about 65% to about 98%; about 75% to about 96%, or about 85% to about 95% has been removed.

[0110] Tailings 72 from the cleaning process 64 are fed to a cleaner scavenger 74 where they undergo further flotation. The cleaner scavenger 74 yields a lead-deficient cleaner scavenger concentrate 76, which is collected and transferred to the cleaning conditioner 44 with the lead-deficient concentrates 42 and 54. The cleaner scavenger 74 also yields lead-rich rougher tailings 78, which are subjected to the solid-liquid separation 58 to remove liquid so as to yield the solid, clean lead concentrate 60.

[0111] The conditioning reagents used for the concentrate enrichment flotation process 24 comprise a collector, a frother, a depressant, and a dispersant. In this embodiment, the collector is a thionocarbamate, which is a poor collector for galena and is therefore suitable for selective flotation of copper sulfosalts in copper-lead concentrates. In this embodiment, the frother is methyl isobutyl carbinol, and the depressant is an ammonium bisulfite solution. The depressant is added to depress lead sulfide flotation, and the method of addition of the depressant is based on achieving a target pH in the pulp. In this embodiment, a caustic starch solution is used as the dispersant. The collector is added to the rougher and cleaning process 64, and may also be added to the scavenger conditioner 48 and the cleaner scavenger 74. The frother is added to the scavenger 52 and the cleaning process 64, and may also be added to the rougher. The depressant and the dispersant are added to the first conditioner 36, the cleaning conditioner 44, and to the cleaning process 64. The dispersant may also be added to the scavenger conditioner 48 and to the cleaner scavenger 74.

[0112] FIG. 3 shows steps of the concentrate enrichment leaching process 26. In the process 26, the first copper concentrate 70 is combined with leach reagents 88 and recycled leach solution 90 from the leach solution recovery process 28, described below, in a repulp/solution preparation process 92 to form a leach feed pulp 94. In this embodiment, the leach reagents 88 are sodium sulfide ( $\text{Na}_2\text{S}$ ) flake having complex from  $.0\text{H}_2\text{O}$  to about  $.9\text{H}_2\text{O}$ , sodium hydroxide (NaOH), and sodium hydrosulfide (NaHS). In this embodiment, NaHS is obtained by passing hydrogen sulfide ( $\text{H}_2\text{S}$ ) evolved downstream during a second acidification process 140 through a caustic scrubber, described below, however in other embodiments, NaHS may be alternatively sourced,

such as being supplied as NaHS flake typically having complex of  $.1\text{H}_2\text{O}$ . If desired, NaHS can be reacted with NaOH to convert it to  $\text{Na}_2\text{S}$  for inclusion in the leach reagents **88**. In the embodiment shown, the leach feed pulp **94** is combined with solids **96** from a wash water acidification process, described below, to yield a leach slurry having a solids content of about 15% to about 30%, and typically about 20%, that is then subjected to a leaching process **98**. During the leaching process **98**, antimony and arsenic are leached in a high pH environment at about atmospheric pressure. The leaching process **98** is carried out at a temperature of about  $95^\circ\text{C}$ . to about  $105^\circ\text{C}$ . using a  $\text{S}^{2-}$  concentration of about 100 to about 120 g/L, and for a time sufficient to achieve greater than about 90% arsenic and antimony extraction, typically about four (4) to about eight (8) hours. The leaching process **98** yields a leach pulp **102** that is subjected to a filtration process **104**, in which solids are removed to yield a leach solution **106**. In this embodiment, the filtration process **104** is performed using a suitable filtration device, such as a recessed plate filter press. Solids **108** filtered by the filtration process **104** are subjected to a sodium hydroxide (NaOH) filtrate wash process **110** to provide protective alkalinity and/or to prevent arsenic and antimony precipitation, so as to yield a solid, second copper concentrate **112** (e.g. a "clean" copper concentrate). The second copper concentrate **112** is substantially free of antimony and arsenic sulfides and is of suitable grade for commercial sale. Typically, at least about 75% of the original antimony and arsenic sulfide content of the mixed sulfide concentrate **22** has been removed; more typically, about 75% to about 99% has been removed; still more typically, about 80% to about 95% has been removed, and most typically about 85% to about 95% has been removed.

[0113] In this embodiment, the wash solution **114** from the filtrate wash process **110** is then subjected to an oxidation process **118**, in which elemental sulfur ( $\text{S}^0$ ) is added to the wash solution **114** at an elevated temperature in order to oxidize ( $\text{As}^{3+}$ ) and ( $\text{Sb}^{3+}$ ) to ( $\text{As}^{5+}$ ) and ( $\text{Sb}^{5+}$ ), respectively, so as to yield an oxidized wash solution **120**. The oxidation process **118** is carried out under about atmospheric pressure at a temperature of about  $65^\circ\text{C}$ . to about  $75^\circ\text{C}$ ., as required for dissolution of elemental sulfur, and for a time of about 0.1 hours to about 1 hour. The oxidized wash solution **120** is then acidified in a first acidification process **122**, in which silicon, aluminum and copper are precipitated to yield an acidified wash slurry **124**. In this embodiment, during the first acidification process **122**, sulfuric acid is added to the oxidized wash solution **120** to reduce the pH to about 9.0 to about 10.0, in order to induce precipitation of the silicon, aluminum and copper. The acidified wash slurry **124** is then subjected to solid-liquid separation **126** to yield a mixed silicon, aluminum and copper precipitate **130** and a solution **132**. The solution **132** is then subjected to a gold recovery process **134**, during which the solution **132** is passed through a strong base ion exchange resin for extraction of gold and/or other precious metals. Solution **138**, which remains after gold recovery process **134**, is then acidified in a second acidification process **140**, in which arsenic and antimony are precipitated as their respective sulfides, and any remaining gold copper, selenium, mercury and other impurities are also precipitated, and in which hydrogen sulfide ( $\text{H}_2\text{S}$ ) gas **144** is evolved. In this embodiment, during the second acidification process **140**, sulfuric acid is added to the solution **138** to reduce the pH to about 3.0 to about 4.0, in order to ensure

precipitation of the arsenic and antimony sulfides. The  $\text{H}_2\text{S}$  gas **144** evolved during the second acidification process **140** is passed through a caustic scrubber (not shown) to yield a sodium sulfide ( $\text{Na}_2\text{S}$ ) or sodium hydrosulfide (NaHS) product, which in the embodiment shown, is combined with leach reagents **88** in the repulp/solution preparation process **92**, for recycling. As will be appreciated, the recycling of reagents reduces the cost of supplying reagents, and/or the cost of destruction of used reagents. The second acidification process **140** yields a slurry **142**, which is subjected to solid-liquid separation **146** to yield the solids **96** and an acidified wash solution **148**. The acidified wash solution **148** is advanced to crystal dissolution **164** where the remaining acid is neutralized, and the solids **96** are combined with the leach feed pulp **94** during the leaching process **98** to releach the contained arsenic and antimony sulfides.

[0114] FIG. 4 shows steps of the leach solution recovery process **28**. In the process **28**, the leach solution **106**, which is rich in both soluble arsenic and soluble antimony, is subjected to an oxidation process **152**, in which elemental sulfur ( $\text{S}^0$ ) is added to the leach solution at an elevated temperature so as to yield an oxidized solution **154**. During the oxidation process **152**, the leach solution is monitored by colorimetry and/or oxidation reduction potential (ORP) to determine the endpoint of oxidation for controlling the addition of elemental sulfur. In this embodiment, the endpoint of oxidation occurs with a color change from yellow-green to orange-red. The oxidation process **152** is carried out under about atmospheric pressure at a temperature of about  $65^\circ\text{C}$ . to about  $75^\circ\text{C}$ ., as required for dissolution of elemental sulfur, and for a time of about 0.1 hours to about 1 hour. The oxidized solution **154** is then subjected, in undiluted form, to a cooling process **156** to crystallize  $\text{Na}_3(\text{As,Sb})\text{S}_4 \cdot x\text{H}_2\text{O}$  solids, where x is typically from about 8 to about 9, so as to yield a slurry **158** comprising the  $\text{Na}_3(\text{As,Sb})\text{S}_4 \cdot x\text{H}_2\text{O}$  solids. In this embodiment, during the cooling process **156**, the oxidized solution **154** is brought to a temperature of at least about  $40^\circ\text{C}$ ., and typically about  $40^\circ\text{C}$ . to about  $45^\circ\text{C}$ ., and is held at this temperature under suitable agitation so as to engender the growth of well-formed crystals, and for a time sufficient to allow crystallization to be complete, typically about one (1) hour to about three (3) hours. The slurry **158** is then subjected to solid-liquid separation **160** to separate the  $\text{Na}_3(\text{As,Sb})\text{S}_4 \cdot x\text{H}_2\text{O}$  solids **162** from the recycle leach solution **90**. In this embodiment, the solid-liquid separation **160** is carried out using a centrifuge, or any filter that will provide suitable separation, and without washing so as to avoid crystal dissolution. The recycle leach solution **90** is combined with the leach reagents **88** in the repulp/solution preparation process **92** of the concentrate enrichment leaching process **26**.

[0115] The solids **162** remaining after the solid-liquid separation **160** are dissolved in water and the acidified wash solution **148** (or wash solution **114**, acidified wash solution **432**, acidified wash solution **538**, acidified wash solution **634** or acidified wash solution **750**, from process **326**, **426**, **526**, **626** or **727**, respectively, described below) during a dissolution process **164** to yield a solution **166** comprising dissolved sodium thioantimonate ( $\text{Na}_3\text{SbS}_4$ ) and dissolved sodium thioarsenate ( $\text{Na}_3\text{AsS}_4$ ). The solution **166** has a combined antimony and arsenic concentration of about 50 g/L to about 100 g/L, depending on water addition. The solution **166** is then transferred to a gold recovery process

**168** in which gold and/or other precious metals are recovered. In this embodiment, during the gold recovery process **168**, the solution **166** is passed through a filter to recover insoluble gold from the dissolution process **164**. Solution **170** remaining after the gold recovery process **168** is then acidified in a first acidification process **172**, in which an antimony sulfide product containing predominantly antimony pentasulfide ( $\text{Sb}_2\text{S}_5$ ) is precipitated to yield a slurry **174** and to evolve hydrogen sulfide ( $\text{H}_2\text{S}$ ) gas **176**. In this embodiment, during the first acidification process **172**, sufficient sulfuric acid is added to the solution **170** to reduce the pH to about 13 to about 7, in order to induce precipitation of typically about 60% to about 80% of the contained antimony as antimony sulfide. After addition of the sulfuric acid, the slurry **174** is passed through a gas stripping tower (not shown), counter current to air, to remove any dissolved  $\text{H}_2\text{S}$  gas. The  $\text{H}_2\text{S}$  gas recovered from the solution is combined with the  $\text{H}_2\text{S}$  gas **176** evolved during the first acidification process **172**. The slurry **174** is then subjected to solid-liquid separation **178** to yield an antimony sulfide precipitate **180** and a solution **182**. The solution **182** is then acidified in a second acidification process **184** to precipitate arsenic and antimony species, which may include generally all of the arsenic and antimony species, so as to yield an acidified slurry **186** and to evolve hydrogen sulfide ( $\text{H}_2\text{S}$ ) gas **188**. In this embodiment, during the second acidification process **184**, sulfuric acid is added to the solution **182** to reduce the pH to about 4.0. The evolved  $\text{H}_2\text{S}$  gas **188** (which may be combined with the  $\text{H}_2\text{S}$  gas **176** above) is passed through a caustic scrubber (not shown) to yield a sodium sulfide ( $\text{Na}_2\text{S}$ ) or sodium hydrosulfide ( $\text{NaHS}$ ) product solution, which is combined with leach reagents **88** in the repulp/solution preparation process **92**, for recycling. The acidified slurry **186** is passed through a gas stripping tower, counter current to air, to remove any dissolved  $\text{H}_2\text{S}$  gas. The  $\text{H}_2\text{S}$  gas recovered from the solution is combined with the  $\text{H}_2\text{S}$  gas **188** evolved during the second acidification process **172**. The acidified slurry **186** is then subjected to a sulfide oxidation process **190**, in which the solution is made more basic through the addition of  $\text{NaOH}$  to dissolve the arsenic and antimony sulfide precipitate in slurry **186**. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is then added to oxidize the dissolved thio-salts. Any suitable oxidizing agent may be used. In this embodiment, sodium hydroxide having a concentration of typically 50 wt % is added until an endpoint pH of from about 10.0 to about 12.0 is reached, after which hydrogen peroxide having a concentration of 30% to 70% is added slowly over a time sufficient to oxidize the dissolved thio-salts completely or nearly completely, typically about 3 hours to about 6 hours. During the sulfide oxidation process **190**, more sodium hydroxide is added to maintain the pH from about 10.0 to about 12.0 to prevent or reduce the formation of elemental sulfur. The sulfide oxidation process **190** is carried out at about atmospheric pressure, and advantageously does not require use of an autoclave. The sulfide oxidation process **190** yields a slurry **192** containing predominantly solid sodium antimony hydroxide ( $\text{NaSb}(\text{OH})_6$ ) and soluble arsenate ( $\text{AsO}_4^{3-}$ ). The slurry **192** is then subjected to solid-liquid separation **194** to remove solids using any combination of thickeners, filters, or other commercially available solid-liquid separation technologies, so as to yield a solid sodium antimony hydroxide product **196** and a residual solution **198**. The sodium antimony hydroxide

product **196** may undergo further processing to produce an antimony-containing product of suitable grade for commercial sale.

[0116] FIG. 5 shows steps of the leach tails stabilization process **30**. In the process **30**, residual solution **198** from the solid-liquid separation **194** (or residual solution **898** or residual solution **998**, from process **828** or **928**, respectively, described below), which has an As:Sb concentration (g/L) ratio of about 10:1 to about 500:1, typically about 20:1 to about 200:1, and more typically about 50:1 to about 100:1, is subjected to a first arsenic solution conditioning process **202** to ensure complete oxidation of arsenic and the dissolved sulfur species. During the first arsenic solution conditioning process **202**, the residual solution **198** is acidified through the addition of sulfuric acid so as to reduce the pH to about 1.5 to about 2.0 at a temperature of about 60° C. to about 80° C., in order to decompose thiosulfates, at least, and possibly other sulfur species. Hydrogen peroxide is then added to oxidize ( $\text{As}^{3+}$ ) to ( $\text{As}^{5+}$ ) and to oxidize soluble, reduced sulfur species to sulfate. The first arsenic solution conditioning process **202** yields a slurry **204** containing predominantly elemental sulfur, with soluble sulfate ( $\text{SO}_4^{2-}$ ) and arsenate ( $\text{AsO}_4^{3-}$ ). The slurry **204** is subjected to solid-liquid separation **206**, so as to yield a mixed solid precipitate **208** comprising predominantly elemental sulfur, and a liquid **210**. The elemental sulfur may be returned for use in the oxidation process **152**. If necessary, the liquid **210** is then subjected to a second arsenic solution conditioning process **212**, in which it is oxidized through the addition of hydrogen peroxide and, optionally, further acidified through the addition of sulfuric acid, to ensure that residual reduced sulfur species are oxidized, so as to yield an oxidized solution **216**. Due to the use of sodium throughout the process, the oxidized solution **216** has a sodium concentration that is higher than that of conventional feed solutions subjected to conventional arsenic stabilization processes. Typically, the sodium concentration of the oxidized solution **216** is at least about 10 g/L; more typically, about 30 g/L to about 70 g/L; still more typically, about 50 g/L to about 60 g/L. During both the first arsenic solution conditioning process **202** and the second arsenic solution conditioning process **212**, the solution is monitored using oxidation reduction potential (ORP). Once an ORP value of greater than about 600 mV ( $\text{Ag}/\text{AgCl}$ ) has been obtained, the oxidized solution **216** is combined with precipitation reagents **218** and solid **234** recycled from downstream processing, described below, in an arsenic stabilization process **220**, so as to yield a stabilized arsenic-containing pulp **222**. In this embodiment, the precipitation reagents **218** comprise sulfuric acid ( $\text{H}_2\text{SO}_4$ ) having a concentration of about 93% to about 98%, a ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) solution having a concentration by weight of about 40% to about 50%, and a lime ( $\text{Ca}(\text{OH})_2$ ) slurry formed by reacting about 75% to about 95% calcium oxide ( $\text{CaO}$ ) solids or calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) solids with water. Additionally, in this embodiment, the arsenic stabilization process **220** is carried out at a temperature of about 80° C. to about 95° C., and at a pH of about 0.8 to about 1.5, in order to control precipitation morphology. The stabilized arsenic-containing pulp **222** containing from about 0.3 g/L to about 2.0 g/L soluble arsenic is then combined with arsenic polish reagents **224** and subjected to an arsenic polish process **226**. In this embodiment, the arsenic polish reagents **224** comprise a ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) solution having a concentration by



weight of about 40% to about 50%, and a lime ( $\text{Ca}(\text{OH})_2$ ) slurry formed by reacting about 75% to about 95% calcium oxide ( $\text{CaO}$ ) solids or calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) solids with water. Additionally, in this embodiment, the arsenic polish process 226 is carried out at a temperature of about 50° C. to about 80° C., and the arsenic polish reagents 224 are added such that the Fe:As ratio is about 3:1 to about 8:1, preferably about 5:1, and such that the pH is about 4 to about 6, preferably about 5 to about 5.5. The arsenic polish process 226 yields a pulp 228 containing less than about 5 mg/L soluble arsenic which is then subjected to solid-liquid separation 232 to yield stabilized arsenic-containing solid 234 and a liquid 236. The solid 234 is removed, and a portion of the solid 234 is returned to the arsenic stabilization process 220 to act as precipitation seed material during the arsenic stabilization process 220. Typically, the portion comprises between about 2% to about 15% by weight of the solid 234, preferably between about 5% to about 10%, and more preferably about 8%. The remaining solid is discharged to disposal 240. The solid 234 comprises stable arsenic compounds, such as ferric arsenate, that are compliant with toxic characteristic leaching procedure (TCLP) standards and are safe for disposal. The liquid 236 is substantially free of arsenic and antimony, and is also safe for disposal 240.

[0117] Other configurations are possible. For example, FIG. 6 shows steps of another embodiment of a concentrate enrichment leaching process, which is generally indicated by reference numeral 326. Process 326 is generally similar to process 26 described above and with reference to FIG. 3. In this embodiment, the wash solution 114 from the sodium hydroxide ( $\text{NaOH}$ ) filtrate wash process 110 is advanced directly to crystal dissolution 164. Additionally, in this embodiment, the leach reagents 88 are sodium sulfide ( $\text{Na}_2\text{S}$ ) flake having complex from  $.0\text{H}_2\text{O}$  to about  $.9\text{H}_2\text{O}$ , and sodium hydroxide ( $\text{NaOH}$ ), which are combined to make a concentrated solution.

[0118] FIG. 7 shows steps of another embodiment of a concentrate enrichment leaching process, which is generally indicated by reference numeral 426. Process 426 is generally similar to process 26 described above and with reference to FIG. 3, but comprises only a single acidification step. In this embodiment, the leach reagents 88 are sodium sulfide ( $\text{Na}_2\text{S}$ ) flake having complex from  $.0\text{H}_2\text{O}$  to about  $.9\text{H}_2\text{O}$ , and sodium hydroxide ( $\text{NaOH}$ ), which are combined to make a concentrated solution. Additionally, in this embodiment, the wash solution 114 from the filtrate wash process 110 is subjected to the oxidation process 118, in which elemental sulfur ( $\text{S}^0$ ) is added to the wash solution 114 at an elevated temperature so as to yield the oxidized wash solution 120. The oxidation process 118 is carried out under the conditions described above, and with reference to FIG. 3. The oxidized wash solution 120 is then acidified in an acidification process 422, in which antimony, silicon, aluminum, copper and gold are precipitated to yield an acidified wash slurry 424. In this embodiment, during the acidification process 422, sulfuric acid is added to the oxidized wash solution 120 to reduce the pH to about 8.5 to about 9.0, in order to induce precipitation of the antimony, silicon, aluminum, copper and gold. The acidified wash slurry 424 is then subjected to solid-liquid separation 428 to yield a mixed antimony, silicon, aluminum, copper and gold bearing precipitate 430 and an acidified wash solution 432. The acidified wash solution 432 is advanced directly to crystal dissolution 164. The mixed antimony, silicon, aluminum,

copper and gold bearing precipitate 430 may be transferred to separate processing (not shown) for recovery of gold.

[0119] In a related embodiment, the oxidation process 118 may alternatively be omitted from the process 426, in which case the wash solution 114 from the filtrate wash process 110 may alternatively be acidified in the acidification process 422.

[0120] FIG. 8 shows steps of another embodiment of a concentrate enrichment leaching process, which is generally indicated by reference numeral 526. Process 526 is generally similar to process 26 described above and with reference to FIG. 3, but comprises only a single acidification step. In this embodiment, the leach reagents 88 are sodium sulfide ( $\text{Na}_2\text{S}$ ) flake having complex from  $.0\text{H}_2\text{O}$  to about  $.9\text{H}_2\text{O}$ , and sodium hydroxide ( $\text{NaOH}$ ), which are combined to make a concentrated solution. Additionally, in this embodiment, the wash solution 114 from the filtrate wash process 110 is subjected to the oxidation process 118, in which elemental sulfur ( $\text{S}^0$ ) is added to the wash solution 114 at an elevated temperature so as to yield the oxidized wash solution 120. The oxidation process 118 is carried out under the conditions described above, and with reference to FIG. 3. The oxidized wash solution 120 is then acidified in an acidification process 522, in which silicon, aluminum and copper are precipitated to yield an acidified wash slurry 524. In this embodiment, during the acidification process 522, sulfuric acid is added to the oxidized wash solution 120 to reduce the pH to about 9.0 to about 10.0, in order to induce precipitation of the silicon, aluminum and copper. The acidified wash slurry 524 is then subjected to solid-liquid separation 528 to yield a mixed silicon, aluminum and copper bearing precipitate 530 and an acidified wash solution 532. The acidified wash solution 532 is then subjected to a gold recovery process 534, during which the solution 532 is passed through a strong base ion exchange resin for extraction of gold and/or other precious metals. Acidified wash solution 538, which remains after gold recovery process 534, is then advanced directly to crystal dissolution 164.

[0121] In a related embodiment, the oxidation process 118 may alternatively be omitted from the process 526, in which case the wash solution 114 from the filtrate wash process 110 may alternatively be acidified in the acidification process 522.

[0122] FIG. 9 shows steps of another embodiment of a concentrate enrichment leaching process, which is generally indicated by reference numeral 626. Process 626 is generally similar to process 26 described above and with reference to FIG. 3, but comprises only a single acidification step. In this embodiment, the wash solution 114 from the filtrate wash process 110 is acidified in an acidification process 622, in which arsenic, antimony, gold, copper, and other elements, are precipitated as a mixture of sulfides and other species to yield an acidified wash slurry 624, and in which hydrogen sulfide ( $\text{H}_2\text{S}$ ) gas 628 is evolved. In this embodiment, during the acidification process 622, sulfuric acid is added to the wash solution 114 to reduce the pH to about 4.0 in order to induce precipitation of the arsenic, antimony, gold, copper, and other elements. The evolved  $\text{H}_2\text{S}$  gas 628 is passed through a caustic scrubber (not shown) to yield a sodium sulfide ( $\text{Na}_2\text{S}$ ) or a sodium hydrosulfide ( $\text{NaHS}$ ) product solution, which in the embodiment shown, is combined with leach reagents 88 in the repulp/solution preparation process 92, for recycling. The acidified wash slurry 624 is then

subjected to solid-liquid separation **630** to yield a mixed sulfide precipitate **632** and an acidified wash solution **634**. The acidified wash solution **634** is advanced to crystal dissolution **164**, and the solids **632** are combined with the leach feed pulp **94** during the leaching process **98**.

[0123] In a related embodiment, the solids **632** may alternatively be advanced to the sulfide oxidation process **190**, for example.

[0124] FIG. 10 shows steps of still another embodiment of a concentrate enrichment leaching process, which is generally indicated by reference numeral **726**. Process **726** is generally similar to process **26** described above and with reference to FIG. 3, but does not comprise an in-line gold recovery process. In this embodiment, the wash solution **114** from the filtrate wash process **110** is subjected to the oxidation process **118**, in which elemental sulfur ( $S^0$ ) is added to the wash solution at an elevated temperature so as to yield the oxidized wash solution **120**. The oxidation process **118** is carried out under the conditions described above, and with reference to FIG. 3. The oxidized wash solution **120** is then acidified in a first acidification process **722**, in which silicon, aluminum, copper and gold are precipitated to yield an acidified wash slurry **724**. In this embodiment, during the first acidification process **722**, sulfuric acid is added to the oxidized wash solution **120** to reduce the pH to about 8.5 to about 9.0, in order to induce precipitation of the antimony, silicon, aluminum, copper and gold. The acidified wash slurry **724** is then subjected to solid-liquid separation **728** to yield a mixed antimony, silicon, aluminum, copper and gold precipitate **730** and an acidified wash solution **732**. The acidified wash solution **732** is then further acidified in a second acidification process **740**, in which arsenic, antimony, residual gold, copper, and other elements, are precipitated as a mixture of sulfides and other species to yield an acidified wash slurry **742**, and in which hydrogen sulfide ( $H_2S$ ) gas **744** is evolved. In this embodiment, during the second acidification process **740**, sulfuric acid is added to the acidified wash solution **732** to reduce the pH to about 4.0 in order to induce precipitation of the arsenic, antimony, gold, copper, and other elements. The evolved  $H_2S$  gas **744** is passed through a caustic scrubber (not shown) to yield a sodium sulfide ( $Na_2S$ ) or sodium hydrosulfide ( $NaHS$ ) product solution, which in the embodiment shown, is combined with leach reagents **88** in the repulp/solution preparation process **92**, for recycling. The acidified wash slurry **742** is then subjected to solid-liquid separation **746** to yield a mixed sulfide precipitate **748** and an acidified wash solution **750**. The acidified wash solution **750** is advanced to crystal dissolution **164**, and the solids **748** are combined with the leach feed pulp **94** during the leaching process **98**.

[0125] In a related embodiment, the oxidation process **118** may alternatively be omitted from the process **726**, in which case the wash solution **114** from the filtrate wash process **110** may alternatively be acidified in the first acidification process **722**.

[0126] FIG. 11 shows steps of another embodiment of a leach solution recovery process, which is generally indicated by reference numeral **828**. Process **828** is generally similar to process **28** described above and with reference to FIG. 4, but comprises only a single acidification process. In this embodiment, solution **170** is acidified in an acidification process **884** to precipitate generally all remaining arsenic and antimony species, so as to yield an acidified slurry **886**

and to evolve hydrogen sulfide ( $H_2S$ ) gas **888**. In this embodiment, during the acidification process **884**, sulfuric acid is added to the solution **170** to reduce the pH to about 4.0. The evolved  $H_2S$  gas **888** is passed through a caustic scrubber (not shown) to yield a sodium sulfide ( $Na_2S$ ) or sodium hydrosulfide ( $NaHS$ ) product solution, which is combined with leach reagents **88** in the repulp/solution preparation process **92**, for recycling. The acidified slurry **886** is passed through a gas stripping tower (not shown), counter current to air, to remove any dissolved  $H_2S$  gas. Any  $H_2S$  gas recovered from the solution is combined with the  $H_2S$  gas **888** from the acidification process **884**. The acidified slurry **886** is then subjected to a sulfide oxidation process **890**, in which the solution is made more basic through the addition of  $NaOH$  to dissolve the arsenic and antimony sulfide precipitate in slurry **186**. Hydrogen peroxide ( $H_2O_2$ ) is then added to oxidize the dissolved thiosalts. Any suitable oxidizing agent may be used. In this embodiment, sodium hydroxide having a concentration of about 50 wt % is added until an endpoint pH of about 10.0 to about 12.0 is reached, after which hydrogen peroxide having a concentration of about 30% to about 70% is added slowly over a time sufficient to oxidize the dissolved thiosalts, which may include complete or nearly complete oxidation of the thiosalts, typically about 3 hours to about 6 hours. During the sulfide oxidation process **890**, more sodium hydroxide is added to maintain the pH from about 10.0 to about 12.0 to prevent formation of elemental sulfur. The sulfide oxidation process **890** is carried out at about atmospheric pressure, and advantageously does not require use of an autoclave. The sulfide oxidation process **890** yields a slurry **892** containing predominantly solid sodium antimony hydroxide ( $NaSb(OH)_6$ ) and soluble arsenate ( $AsO_4^{-3}$ ). The slurry **892** is then subjected to solid-liquid separation **894** to remove solids using any combination of thickeners, filters, or other commercially available solid-liquid separation technologies, so as to yield a solid sodium antimony hydroxide product **896** and a residual solution **898**. The sodium antimony hydroxide product **896** may undergo further processing to produce an antimony-containing product of suitable grade for commercial sale. The residual solution **898** is advanced to an arsenic solution conditioning process, such as the first arsenic solution conditioning process **202**, for example.

[0127] FIG. 12 shows steps of another embodiment of a leach solution recovery process, which is generally indicated by reference numeral **928**. Process **928** is generally similar to process **28** described above and with reference to FIG. 4, but does not comprise any acidification processes. In this embodiment, solution **170** is subjected to a sulfide oxidation process **990**, in which sodium hydroxide solution is added to control pH so as to prevent formation of elemental sulfur and thereby avoid contamination of the solids, and hydrogen peroxide ( $H_2O_2$ ) is added to oxidize the dissolved thiosalts. Any suitable oxidizing agent may be used. In this embodiment, sodium hydroxide having a concentration of about 50 wt % is added to control pH at about 10.0 to about 12.0, and hydrogen peroxide having a concentration of about 30% to about 70% is added slowly over a time sufficient to oxidize the dissolved thiosalts completely or nearly completely, typically about 3 hours to about 6 hours. The sulfide oxidation process **990** is carried out at about atmospheric pressure, and advantageously does not require use of an autoclave. The sulfide oxidation process **990** yields a slurry

**992** containing predominantly solid sodium antimony hydroxide ( $\text{NaSb}(\text{OH})_6$ ) and soluble arsenate ( $\text{AsO}_4^{-3}$ ). The slurry **992** is then subjected to solid-liquid separation **994** to remove solids using any combination of thickeners, filters, or other commercially available solid-liquid separation technologies, so as to yield a solid sodium antimony hydroxide product **996** and a residual solution **998**. The sodium antimony hydroxide product **996** may undergo further processing to produce an antimony-containing product of suitable grade for commercial sale. The residual solution **998** is advanced to an arsenic solution conditioning process, such as the first arsenic solution conditioning process **202**, for example.

[0128] FIG. 13 shows steps of another embodiment of a leach tails stabilization process, which is generally indicated by reference numeral **1030**. Process **1030** is generally similar to process **30** described above and with reference to FIG. 5, but comprises a single arsenic solution conditioning step. In this embodiment, the residual solution **198** from the solid-liquid separation **194** is subjected to an arsenic solution conditioning process **1002**, in which it is oxidized prior to pH adjustment through the addition of hydrogen peroxide to ensure that all residual arsenite ( $\text{As}^{3+}$ ) and reduced sulfur species are fully oxidized. In this embodiment, elemental sulfur formation is limited or absent. The solution is then acidified through the addition of sulfuric acid so as to reduce the pH to about 1.5 to about 2.0, so as to yield an acidified oxidized solution **1004**. Due to the use of sodium throughout the process, the oxidized solution **1004** has a sodium concentration that is higher than that of conventional feed solutions subjected to conventional arsenic stabilization processes. Typically, the sodium concentration of the acidified oxidized solution **1004** is at least about 10 g/L; more typically, about 30 g/L to about 70 g/L; still more typically, about 50 g/L to about 60 g/L. During the arsenic solution conditioning process **1002**, the solution may be monitored using oxidation reduction potential (ORP), and the process may be carried out until a desired ORP value (greater than about 600 mV (Ag/AgCl) in the acidified solution), has been obtained. After the arsenic solution conditioning process **1002**, the acidified oxidized solution **1004** is combined with precipitation reagents **218** and solid **234** recycled from downstream processing in the arsenic stabilization process **220**, which has been described above and with reference to FIG. 5.

[0129] As will be appreciated, the process for separation of metal sulfides is not limited to that described above, and in other embodiments the process may comprise one or more of the following sub processes: the concentrate enrichment flotation process **24**, the concentrate enrichment leaching process **26**, the leach solution recovery process **28**, and the leach tails stabilization process **30**.

[0130] For example, the process comprises the concentrate enrichment flotation process **24** described above, together with one or more other sub processes for processing and/or removal of copper, antimony and/or arsenic sulfides. In another related embodiment, the process comprises the concentrate enrichment flotation process **24** and the concentrate enrichment leaching process **26** described above, together with other sub processes for processing and/or removal of antimony and/or arsenic sulfides. In another related embodiment, the process comprises the concentrate enrichment flotation process **24** and the leach solution recovery process **28** described above, together with other

sub processes for processing and/or removal of copper, antimony and/or arsenic sulfides. In another related embodiment, the process comprises the concentrate enrichment flotation process **24** and the leach tails stabilization process **30** described above, together with other sub processes for processing and/or removal of copper, antimony and/or arsenic sulfides. In another related embodiment, the process comprises the concentrate enrichment flotation process **24** and any two (2) of the concentrate enrichment leaching process **26**, the leach solution recovery process **28**, and the leach tails stabilization process **30** described above, together with one or more other sub processes for processing and/or removal of copper, antimony and/or arsenic sulfides.

[0131] In other embodiments, the process comprises the concentrate enrichment leaching process **26** described above, together with one or more other sub processes for processing and/or removal of lead, antimony and/or arsenic sulfides. In one related embodiment, the process comprises the concentrate enrichment leaching process **26** and the leach solution recovery process **28** described above, together with other sub processes for processing and/or removal of lead, antimony and/or arsenic sulfides. In another related embodiment, the process comprises the concentrate enrichment leaching process **26** and the leach tails stabilization process **30** described above, together with other sub processes for processing and/or removal of lead, copper, antimony and/or arsenic sulfides. In another related embodiment, the process comprises the concentrate enrichment leaching process **26** and any two (2) of the concentrate enrichment flotation process **24**, the leach solution recovery process **28**, and the leach tails stabilization process **30** described above, together with one or more other sub processes for processing and/or removal of lead, antimony and/or arsenic sulfides.

[0132] In other embodiments, the process comprises the leach solution recovery process **28** described above, together with one or more other sub processes for processing and/or removal of lead, copper, antimony and/or arsenic sulfides. In one related embodiment, the process comprises the leach solution recovery process **28** and the leach tails stabilization process **30** described above, together with other sub processes for processing and/or removal of lead, copper, antimony and/or arsenic sulfides. In another related embodiment, the process comprises the leach solution recovery process **28** and any two (2) of the concentrate enrichment flotation process **24**, the concentrate enrichment leaching process **26** and the leach tails stabilization process **30** described above, together with one or more other sub processes for processing and/or removal of lead, copper, antimony and/or arsenic sulfides.

[0133] In other embodiments, the process comprises the leach tails stabilization process **30** described above, together with one or more other sub processes for processing and/or removal of lead, copper, antimony and/or arsenic sulfides.

[0134] As will be appreciated, the process for separation of metal sulfides is not limited to the specific metal sulfide embodiments described herein, but may be applied to any suitable separation of metal sulfide(s), including at least one sulfide having at least one metal and/or at least one semi-metal with use of the suitable process step(s) described herein.

[0135] Although various conditions and reagents (e.g. acids, bases, oxidizing agents etc.) are used, various changes and modifications may be made.

**[0136]** For example, although in embodiments described above, hydrogen peroxide is used as an oxidizing agent, in other embodiments, other oxidizing agents may alternatively be used, such as metal catalyzed quinones, including metal catalyzed hydroquinones and any other precursors that may generate hydrogen peroxide. As an example, copper catalyzed hydroquinone may alternatively be used as an oxidizing agent instead of, or in combination with, hydrogen peroxide. Those skilled in the art will appreciate that still other oxidizing agents may be used.

**[0137]** Although in the embodiments described above, the leach solution is monitored during the oxidation process by colorimetry to determine the endpoint of oxidation, in other embodiments, the leach solution may alternatively be monitored by another suitable method to determine the endpoint of oxidation.

**[0138]** Although in the embodiments described above, the frother is methyl isobutyl carbinol, in other embodiments, any frother(s) that are known in the art, which give(s) the recovery of the desired minerals, may alternatively be used. Furthermore, blends of such frothers may also be used.

**[0139]** Although in the embodiments described above, the collector is a thionocarbamate, in other embodiments, any collector that provides sulfosalt (e.g. copper sulfosalt) flotation may alternatively be used. For example, alkyl thionocarbamates and/or allyl alkyl thionocarbamates, including short- and long-chained alkyl thionocarbamates and allyl alkyl thionocarbamates, may be used.

**[0140]** Although in the embodiments described above, the depressant is an ammonium bisulfite solution, in other embodiments, any agent that depresses the flotation of galena in the presence of sulfosalts (e.g. copper sulfosalts) may alternatively be used. Suitable depressants include sulfite salts, such as sulfites, bisulfites, and metabisulfites.

**[0141]** Although in the embodiments described above, the dispersant is a caustic starch solution, in other embodiments, any agent that disperses sulfides may alternatively be used. It is understood that a caustic starch solution may include naturally occurring starch and/or synthetic starch, combined with any suitable base, such as sodium hydroxide.

**[0142]** Although in the embodiments described above, the gold recovery process comprises using a strong base ion exchange resin for extraction of gold and/or other precious metals, in other embodiments, the gold recovery process may alternatively comprise use of a precipitation process for extraction of gold and/or other precious metals. Other known precious metal recovery processes may also be used.

**[0143]** Although in the embodiments described above, the solids filtered by the filtration process are subjected to a sodium hydroxide (NaOH) filtrate wash process so as to yield a wash solution, in other embodiments, the solids filtered by the filtration process may alternatively be washed with another solution or with water, so as to yield the wash solution.

**[0144]** In understanding the scope of the present application, the term “comprising” and its derivatives, as used herein, are intended to be open ended terms that specify the presence of the stated features, elements, components, groups, integers, and/or steps, but do not exclude the presence of other unstated features, elements, components, groups, integers and/or steps. The foregoing also applies to words having similar meanings such as the terms, “including”, “having” and their derivatives. It will be understood that any aspects described as “comprising” certain compo-

nents may also “consist of” or “consist essentially of,” wherein “consisting of” has a closed-ended or restrictive meaning and “consisting essentially of” means including the components specified but excluding other components except for materials present as impurities, unavoidable materials present as a result of processes used to provide the components, and components added for a purpose other than achieving the technical effect of the invention.

**[0145]** Terms of degree such as “about” and “approximately” as used herein mean a reasonable amount of deviation of the modified term such that the end result is not significantly changed. These terms of degree should be construed as including a deviation of at least  $\pm 5\%$  of the modified term if this deviation would not negate the meaning of the word it modifies.

**[0146]** When introducing elements disclosed herein, the articles “a”, “an” and “the” are intended to mean that there are one or more of the elements.

**[0147]** The above disclosure generally describes the present invention. A more complete understanding can be obtained by reference to the following specific Examples. The Examples are described solely for purposes of illustration and are not intended to limit the scope of the invention. Changes in form and substitution of equivalents are contemplated as circumstances may suggest or render expedient. Although specific terms have been employed herein, such terms are intended in a descriptive sense and not for purposes of limitation.

## EXAMPLES

### Example 1

**[0148]** In Examples 1 to 3, “locked cycle” flotation tests were performed to evaluate the removal and separation efficiency of arsenic and antimony containing sulfosalts from the mixed sulfide concentrate.

**[0149]** In this example, the test was performed on a high copper feed concentrate using four locked cycles with a rougher and three stages of cleaning. The collector was a thiocarbamate (Aero A5100), the depressant was sodium metabisulfite (SMBS), and the dispersant was a caustic starch solution.

**[0150]** The results of the test are shown in Table 1. About 89% of the lead reported to the lead concentrate, while about 80% of the copper, about 82% of the arsenic and about 91% of the antimony reported to the copper concentrate.

TABLE 1

Assays	Mass, %	Cu, %	As, %	Sb, %	Pb, %
Pb—Cu bulk conc.	100	30.0	8.3	7.9	24.2
Cu conc.	63	38.5	11.0	14.7	3.9
Pb conc.	37	15.7	4.1	2.3	51.8
Distribution, %	—	Cu	As	Sb	Pb
Pb—Cu bulk conc.	100	100	100	100	100
Cu conc.	63	80	82	91	11
Pb conc.	37	20	18	9	89

### Example 2

**[0151]** In this example, a “locked cycle” flotation test was performed on a lower copper feed concentrate than the

concentrate of Example 1, using six locked cycles with a rougher and three stages of cleaning. In this example, the collector was Aero A5100, the depressant was SMBS, and the dispersant was a caustic starch solution.

[0152] The results of this test are shown in Table 2. About 99% of the lead reported to the lead concentrate, while about 78% of the copper, about 84% of the arsenic and about 74% of the antimony reported to the copper concentrate.

TABLE 2

Assays	Mass, %	Cu, %	As, %	Sb, %	Pb, %
Pb—Cu bulk conc.	100	6.5	1.1	1.8	57.8
Cu conc.	14	35.4	7.5	12.6	3.6
Pb conc.	86	1.7	0.2	0.7	67.3
Distribution, %	—	Cu	As	Sb	Pb
Pb—Cu bulk conc.	100	100	100	100	100
Cu conc.	14	78	84	74	1
Pb conc.	86	22	16	26	99

## Example 3

[0153] In this example, a “locked cycle” flotation test was performed on a similar feed material to Example 2, using six locked cycles with a rougher and three stages of cleaning. In this example, the collector was Aero A5100, the depressant was ammonium bisulfite, and the dispersant was a caustic starch solution.

[0154] The results of this test are shown in Table 3. About 97% of the lead reported to the lead concentrate, while about 84% of the copper, about 86% of the arsenic and about 81% of the antimony reported to the copper concentrate.

TABLE 3

Assays	Mass, %	Cu, %	As, %	Sb, %	Pb, %
Pb—Cu bulk conc.	100	6.3	1.2	3.7	56.2
Cu conc.	19	27.9	5.5	15.4	9.4
Pb conc.	81	1.2	0.2	0.8	62.3
Distribution, %	—	Cu	As	Sb	Pb
Pb—Cu bulk conc.	100	100	100	100	100
Cu conc.	19	84	86	81	3
Pb conc.	81	16	14	19	97

## Example 4

[0155] In Examples 4 and 5, a locked cycle test was performed using repulp/solution preparation process 92, leaching process 98, filtration process 104, filtrate wash process 110, oxidation process 152, crystallization process 156, and solid-liquid separation 160, and with solution 90 being returned to the repulp/solution preparation process 92 for the next cycle. Twenty six cycles were performed in total. Two concentrate samples were used in this test, namely Concentrate 1 (cycles 1 to 18) and Concentrate 2 (cycles 19 to 26), with each concentrate sample comprising 1 kg of first copper concentrate from the concentrate enrichment flotation process 24. More specifically, Concentrate 1 was a composite sample of twelve (12) individual concentrates. The twelve (12) individual concentrates used to generate

Concentrate 1 were determined to contain arsenic and antimony primarily as tetrahedrite and tennantite, with minor amounts of bourmonite, freibergite, boulangerite and enargite being present. The compositions of Concentrate 1 and Concentrate 2 are provided in Table 4.

[0156] During repulp/solution preparation process 92, each concentrate was combined with about 4 kg of leach solution (specifically, fresh leach solution for the first cycle, and recycled leach solution from solid-liquid separation 160 for the subsequent cycles), to make a slurry with about 20 wt % solids. The leach solution recycled from solid-liquid separation 160 was analyzed and weighed, and the required amounts of sodium sulfide ( $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$ ), sodium hydroxide (NaOH) and water were added to yield a solution containing about 120 g/L sulfide and about 40 g/L sodium hydroxide. [0157] The slurry was then heated to about 100° C. and held at that temperature for about six hours to carry out leaching process 98. After the six hours, the slurry was filtered, and the primary filtrate was recovered and kept above about 70° C. prior to oxidation process 152. The solids were washed, during filtrate wash process 110, with about 1.5 L of water containing about 0.05 M NaOH using a two stage counter current wash procedure.

[0158] Chemical analysis results of the two composite concentrate samples are shown in Table 4. About 98% of the arsenic and about 96% of the antimony was leached from the concentrate samples.

TABLE 4

Element	Unit	Concentrate 1			Concentrate 2		
		Feed	Residue	Extraction	Feed	Residue	Extraction
total mass	kg	18.0	15.1	16%	8.0	7.0	13%
As	wt %	7.6	0.13	98%	6.0	0.14	98%
Sb	wt %	10.2	0.53	96%	11.1	0.54	96%
Cu	wt %	29.0	33.8	<5%	30.7	35.6	<5%
Pb	wt %	16.1	18.4	<5%	9.5	11.0	<5%

## Example 5

[0159] In this example, the primary filtrate (leach solution 106) recovered after each leach cycle in Example 4 and kept at above about 70° C., was subjected to oxidation process 152, during which elemental sulfur was added until the color changed from yellow-green to orange-red. ORP values were observed to increase by about 150 mV, which indicated that ORP could have readily been used to measure the endpoint of oxidation.

[0160] Following oxidation, the solution was cooled to about 40° C. and held at that temperature for about 30 to about 60 minutes during crystallization process 156, to allow crystallization of the soluble arsenic and antimony as sodium thioarsenate and sodium thioantimonate. For the 26 cycles performed in the test, about 19.15 kg of wet crystals were recovered assaying about 6.2 wt % arsenic and about 12.1 wt % antimony. After crystallization, the solution 90 typically assayed about 30 to about 40 g/L arsenic and about 5 to about 15 g/L antimony.

## Example 6

[0161] In this example, a test was carried out in which about 200 g of crystals was dissolved in about 600 g of

water, in order to determine the ability to selectively precipitate antimony sulfide ( $\text{Sb}_2\text{S}_5$ ) from the dissolved crystals. Acid was added until precipitation was observed, at which point the solution was filtered and the precipitate analyzed. A further about 5 mL of acid was then added to the filtrate and, after a short equilibration period, the solids were again removed by filtration; this procedure was repeated until the pH dropped below about 5.0.

**[0162]** The results of this test are shown in Table 5. About 63% of the antimony was precipitated at an arsenic grade of about 0.5 wt %, while about 92% of the antimony was precipitated at an arsenic grade of about 1.0 wt %.

TABLE 5

	Sample							
	1	2	3	4	5	6	7	8
pH	7.2	7.8	7.2	7.2	7.4	7.2	6.9	2.9
Cum. solids mass (g)	1.8	3.2	4.7	6.3	7.7	9.3	9.6	15.3
Cum. As assay (wt %)	0.37	0.40	0.44	0.50	0.57	0.98	1.25	16.2
Cum. Sb assay (wt %)	51.5	50.4	49.5	48.7	47.7	48.3	48.0	31.9
Cum. As pptn (%)	0.3	0.5	0.8	1.3	1.8	3.7	4.9	100
Cum. Sb pptn (%)	18.7	33.3	48.2	62.8	75.6	92.4	95.3	100

## Example 7

**[0163]** In this example, the crystals generated in the locked cycle test of Examples 4 and 5 were subjected to first acidification process 172 to generate a sulfide precipitate containing predominantly antimony sulfide ( $\text{Sb}_2\text{S}_5$ ). Here, about five (5) kg of wet crystal was dissolved in about 15 L of water, and the resulting solution was filtered and acidified with concentrated sulfuric acid. After completing acid addition, the slurry was sparged for about 30 minutes to remove dissolved hydrogen sulfide gas. Throughout the test, air was pulled through the reactor headspace and was released to atmosphere via a single stage scrubber filled with about 50% sodium hydroxide solution.

**[0164]** As the antimony started to precipitate, the pH and ORP were observed to become stable. As will be understood, the system was buffered at this pH by the  $\text{NaHS}/\text{H}_2\text{S}$  equilibrium and the slow rate of acid addition. After acid had been added, the pH moved back towards about pH 7 as the system returned to equilibrium.

**[0165]** Following acidification, the slurry was subjected to filtration. Solids recovered after the filtration assayed about 40 wt % antimony, about 33.5 wt % sulfur, and about 1.6 wt % arsenic. Approximately 65% of the antimony and approximately 5% of the arsenic was recovered from the feed solution.

## Example 8

**[0166]** In this example, about 200 g of crystal was dissolved in about 600 mL of water. After filtration, the solution was subjected to sulfide oxidation process 990, in which about 30% hydrogen peroxide was added to the solution until the target ORP was reached. The sulfide oxidation process was carried out both with pH control at pH of about 10, and without any pH control. The precipitate formed

during each test was separated from the solution, washed and analyzed. The results are shown in Table 6. The results indicate that pH control was important in limiting elemental sulfur precipitation into the product.

TABLE 6

	Test #1	Test #2
pH Control at 10 Feed Solution	No	Yes
Arsenic (g/L)	17	17
Antimony (g/L)	35	28
Final Solution		
Arsenic (g/L)	13	—
Antimony (g/L)	0.2	—
Solids Product		
Arsenic (wt %)	0.5	0.7
Antimony (wt %)	38	48
Sulfur (wt %)	24	1
Sodium (wt %)	6	10

## Example 9

**[0167]** Prior to arsenic stabilization, the arsenic solution (solution 198) is conditioned to ensure all of the arsenic and sulfur species are fully oxidized. In this example, an arsenic solution was acidified to a pH less than about 2.0 at about 80° C. The acidification generated elemental sulfur from decomposition of thiosulfate in the solution. Hydrogen peroxide was then added to increase the ORP to above approximately 600 mV, at which point oxidation of the solution was essentially complete, and therefore that the oxidized solution was a suitable feed for the arsenic stabilization process 220.

## Example 10

**[0168]** In this example, a continuous arsenic stabilization test was run on a solution generated by processing dissolved crystal from the locked cycle test of Examples 4 and 5 through first acidification process 172, sulfide oxidation process 190 and arsenic solution conditioning 1002. Ferric sulfate was then added to the acidified oxidized solution 1004 (hereafter the “feed solution”, in this example) to achieve a ferric to arsenic molar ratio of about 1.05. Analysis of the feed solution showed about 11 g/L arsenic, about 9 g/L iron, and about 60 g/L sodium. In this example, the sodium concentration in the solution was much higher than in conventional feed solutions for conventional arsenic stabilization processes due to the existence of sodium in the crystals, and due to the further addition of sodium hydroxide throughout the process.

**[0169]** The test was run continuously for about 26 hours, and included three stages of arsenic precipitation followed by one stage of arsenic polish. Each stage was carried out in a respective reactor. The operating conditions were as follows:

**[0170]** Stage 1 precipitation: about 120 minutes retention at about 90° C., pH about 1.20 and seed concentration of about 80 g/L;

**[0171]** Stage 2 precipitation: about 120 minutes retention at about 90° C., pH about 1.40;

**[0172]** Stage 3 precipitation: about 120 minutes retention at about 90° C., pH about 1.50;

[0173] Stage 4 polish: about 60 minutes retention, with ferric sulfate solution continuously added to maintain a ferric to arsenic molar ratio of about 5 at about 60° C., pH about 5.5.

[0174] During the test, about 6.3 L of feed solution was treated. The polish slurry discharge was collected and combined with contents of the polish reactor at the end of the test, to constitute a discharge composite sample.

[0175] Solution profile sampling was conducted every two hours. The results showed consistent operation once equilibrium had been established, with the arsenic concentration being reduced from about 11 g/L in the feed solution to about 2.5 g/L in the first reactor, to about 0.9 g/L in the second reactor, to about 0.5 g/L in the third reactor. The arsenic concentration in the polish slurry discharge was less than about 2 mg/L. At the end of the test, the discharge composite sample was assayed and was found to contain about 6.4 wt % arsenic, about 6.0 wt % iron, and only about 0.2 wt % sodium. The solids passed TCLP for arsenic with an assay of less than 1.0 mg/L (target: less than about 5 mg/L).

[0176] Although embodiments have been described above with reference to the accompanying drawings, those of skill in the art will appreciate that variations and modifications may be made without departing from the scope thereof as defined by the appended claims.

[0177] The description as set forth is not intended to be exhaustive or to limit the scope of the invention. Many modifications and variations are possible in light of the above teaching without departing from the spirit and scope of the following claims. It is intended that the scope of the present invention be defined by the claims appended hereto, giving full cognizance to equivalents in all respects.

What is claimed is:

1. A process for separation of antimony and arsenic from a leach solution comprising soluble antimony and arsenic, the process comprising:

oxidizing the soluble antimony and arsenic in the leach solution so as to reach an oxidation end point determined by at least one of wavelength monitoring and oxidation reduction potential (ORP) monitoring, to yield soluble antimony and arsenic thiosalts; and

oxidizing the soluble antimony and arsenic thiosalts to yield an antimony precipitate and an arsenic solution.

2. The process of claim 1, wherein antimony and arsenic are present in the leach solution in a molar ratio of about 0.5:1 to about 1.5:1.

3. The process of claim 2, wherein antimony and arsenic are present in the leach solution in a molar ratio of about 1:1.

4. The process of claim 1, wherein the leach solution comprises a major amount of arsenic relative to antimony.

5. The process of claim 1, wherein the leach solution comprises a major amount of antimony relative to arsenic.

6. The process of claim 1, wherein said oxidizing the soluble antimony and arsenic in the leach solution comprises oxidizing with elemental sulfur.

7. The process of claim 1, further comprising:

removing the soluble antimony and arsenic thiosalts from the leach solution by crystallization.

8. The process of claim 7, further comprising:

recovering the leach solution for recycling.

9. The process of claim 7, wherein said removing comprises cooling the leach solution to induce the crystallization.

10. The process of claim 9, wherein said cooling is controlled to avoid crystallization of alkali metal sulfide.

11. The process of claim 7, wherein said crystallization comprises forming thioarsenate and thioantimonate salts.

12. The process of claim 7, further comprising: dissolving crystals formed by said crystallization to yield the soluble antimony and arsenic thiosalts.

13. The process of claim 1, wherein said oxidizing the soluble antimony and arsenic thiosalts comprises using an oxidizing agent.

14. The process of claim 13, wherein said oxidizing agent is hydrogen peroxide and/or a metal catalyzed hydroquinone.

15. The process of claim 1, wherein said oxidizing the soluble antimony and arsenic thiosalts is carried out at about atmospheric pressure.

16. The process of claim 1, further comprising:

prior to said oxidizing the soluble antimony and arsenic thiosalts, acidifying a solution comprising the soluble antimony and arsenic thiosalts to precipitate arsenic and antimony species as a slurry; and

dissolving the precipitated arsenic and antimony species through addition of base to the slurry, wherein said oxidizing comprises oxidizing the dissolved arsenic and antimony species.

17. The process of claim 1, further comprising:

prior to said oxidizing the soluble antimony and arsenic thiosalts, acidifying a solution comprising the soluble antimony and arsenic thiosalts to precipitate an additional antimony sulfide product as a slurry;

separating the additional antimony sulfide product from the slurry;

acidifying the slurry to precipitate arsenic and antimony species; and

dissolving the precipitated arsenic and antimony species through addition of base to the slurry,

wherein said oxidizing comprises oxidizing the dissolved arsenic and antimony species.

18. The process of claim 17, wherein the additional antimony sulfide product comprises antimony pentasulfide.

19. The process of claim 16, wherein hydrogen sulfide gas is produced and the hydrogen sulfide gas is passed through a caustic scrubber.

20. The process of claim 19, wherein a sodium sulfide product or a sodium hydrosulfide product is formed.

21. The process of claim 1, wherein said antimony precipitate comprises sodium antimony hydroxide.

22. The process of claim 1, wherein the arsenic solution comprises soluble arsenate.

23. The process of claim 1, further comprising:

forming a stable arsenic compound from the arsenic solution.

24. The process of claim 23, wherein said forming further comprises:

returning a portion of the stable arsenic compound to said forming to act as precipitation seed material during said forming.

25. The process of claim 23, further comprising, prior to said forming:

acidifying the arsenic solution to decompose thiosulfates, to yield an acidified solution;

oxidizing the acidified solution to oxidize residual As<sup>3+</sup> to As<sup>5+</sup> and reduced sulfur species to sulfates, to yield a slurry comprising elemental sulfur;

separating elemental sulfur from the slurry to yield a liquid; and  
oxidizing the liquid to oxidize residual reduced sulfur species, to yield an oxidized solution,  
wherein said forming comprises forming the stable arsenic compound from the oxidized solution.

**26.** The process of claim **25**, further comprising using the elemental sulfur for use as an oxidizing agent for said oxidizing of the leach solution.

**27.** The process of claim **23**, further comprising, prior to said forming:

oxidizing the arsenic solution to oxidize residual  $\text{As}^{3+}$  to  $\text{As}^{5+}$  and reduced sulfur species to sulfates, to yield an oxidized solution; and  
acidifying the oxidized solution to yield an acidified oxidized solution,  
wherein forming comprises forming the stable arsenic compound from the acidified oxidized solution.

**28.** The process of claim **23**, wherein the stable arsenic compound comprises ferric arsenate.

**29.** The process of claim **23**, wherein the stable arsenic compound is compliant with toxic characteristic leaching procedure (TCLP) standards.

\* \* \* \* \*