

METHOD OF REFINING PRECIOUS METALS

CROSS REFERENCE TO RELATED APPLICATION

5 [0001] This application claims priority to United States Provisional Patent Application number US 63/609,715, filed Dec 13, 2023, the entire contents of which are hereby incorporated by reference

FIELD

10 [0002] The present disclosure relates generally to methods for refining precious metals.

BACKGROUND

15 [0003] Precious metals are a group of elements in the periodic table that includes gold (Au) and the platinum group metals (PGMs) - platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os).

20 [0004] The average concentration of gold in Earth's crust is 0.005 ppm (parts per million). Gold ore deposits having a concentration of 0.5 ppm or higher are considered to be economically recoverable. Due to its limited sources, gold recovery not only from ores, but also from secondary sources has become more and more important during the last decades. The annual production of gold from the gold mining industry is more than 2500 to 3300 tonnes worldwide. In addition, about 900 to 1178 tonnes of secondary gold is recovered from different sources such as but not limited to anode slime and jewelry, dentistry and electronic scraps. PGM ore deposits are generally found with an average concentration of 2-10 ppm (g/t), with hundreds of tonnes of PGMs being produced worldwide from mining and recycled sources
25 (e.g., in 2018, approximately 606.5 tonnes of PGMs were produced).

30 [0005] Precious metals are used in a wide variety of areas due to their unique properties, such as strong catalytic properties, thermal stability, resistance to corrosion, and high melting points. For example, platinum-group metals such as palladium, platinum, and rhodium are used as metallic catalysts in catalytic converters for reduction of harmful gases from vehicle exhaust emissions. Further, gold, palladium, platinum, and rhodium are used in jewelry, electrical and electronics industry (e.g., in multilayer ceramic capacitors and in computer hard disks to increase storage capacity), as well as investments in the form of bars and coins.

[0006] Extraction of precious metals from materials can involve hydrometallurgical routes that comprise the steps of acid or caustic leaching for selective dissolution of precious metals using aqua regia for leaching. Generally, the pregnant leach solution is then separated and purified for enrichment of metal content whereby impurities are removed as gangue materials. Isolating the precious metals can be conducted through solvent extraction, adsorption, and/or ion exchange enrichment processes; and recovery of the metals from solution can be conducted through electrorefining (electrometallurgy) or chemical reduction processes. Leaching solutions such as halides, cyanides, thiourea, and thiosulfates are used for leaching of precious metals from their primary ores.

[0007] There are limitations to hydrometallurgical processes, such as: (i) being a slow and time consuming process; (ii) loss of precious metals during mechanical processing of waste (e.g., loss of upwards of 20%); (iii) using toxic chemicals such as cyanide as a leachant, thereby requiring high safety standards and protocols, to avoid environmental contamination and human health risks; and (iv) there being a risk of further loss of precious metal during subsequent dissolution and separation steps, which impacts the overall metal recovery.

[0008] Extraction of precious metals from materials can also involve pyrometallurgical techniques, which include conflagrating, smelting in a plasma arc furnace, drossing, sintering, melting, and varied reactions in a gas phase at high temperatures. Generally, pyrometallurgical processes include the steps of liberation, separation/upgrading, and purification, which are similar to those of hydrometallurgical processes. However, in contrast to hydrometallurgical processes, pyrometallurgical processes do not rely on leaching but rather smelting in furnaces at high temperatures. Precious metals may therefore be sorted based on chemical and metallurgical properties.

[0009] Limitations of pyrometallurgical processes include: (i) not being able to recover and/or recycle plastics, as they are sometimes used in place of coke as a fuel source; (ii) reduced iron and aluminum recovery, as they end up as oxides in slag phases; (iii) generation of hazardous emissions, such as dioxins, during smelting of certain feed materials (e.g, halogenated flame retardants) requiring special installations to minimize environmental pollution; (iv) high costs of implementing integrated e-waste recycling plants that maximize recovery of valuable metals while also controlling hazardous gas emissions and protecting the environment; (v) burning of fine dust generated from non-metallic portions of e-wastes should be controlled and/or minimized to avoid the health risk posed by fine dust particles; (vi) only a partial recovery and purity of precious metals are affected by pyrometallurgical routes, therefore requiring

additional hydrometallurgical and electrochemical techniques to extract pure metals; and (vii) managing smelting and refining is challenging due to the complexity of feed materials and the thermodynamics of possible reactions.

5 [0010] Once extracted, precious metals may be refined. Refining is the process in which impurities are removed from precious metals, which may result in metals having a purity of $\geq 99\%$. A means of refining precious metal, such as gold, involve using a combination of the Miller and Wohlwill processes. In the Miller process, gold of 95% purity and below is melted down and chlorine gas is bubbled through the molten metal. Impurities bind to the chlorine and are collected as slag, leaving 99.5% pure gold to be poured into an anode mold to continue to the Wohlwill process. In the Wohlwill process, the gold is purified electrolytically in a bath of chloroauric acid. 10 Limitations of these processes include incurring a significant cost for shipping and smelting the precious metal.

SUMMARY

15 [0011] In one or more embodiments of the present disclosure, there is provided:

1. A method of refining a precious metal, the method comprising contacting the precious metal with a refining solution under conditions to solubilize the precious metal, the refining solution comprising an acid, an oxidant, a ligand source, and a partially water-miscible or water-miscible organic solvent; and forming a leach solution comprising leached precious metal. 20
2. The method of embodiment 1, further comprising contacting the leach solution with a reductant, and precipitating the leached precious metal.
3. The method of any preceding embodiment, wherein the reductant comprises sodium metabisulfite, Fe(II)Cl_2 , ascorbic acid, oxalic acid, hydrazine, hydrazine hydrochloride, 25 hydroxylamine, hydroxylamine hydrochloride, or a combination thereof.
4. The method of any preceding embodiment, further comprising contacting the precipitated precious metal with a rinse solution for dissolving contaminants, the rinse solution comprising a complexation reagent; and forming a refined precious metal.
5. The method of any preceding embodiment, wherein the complexation reagent 30 comprises a thiourea, a thiosulfate, or a combination.
6. The method of any preceding embodiment, wherein the rinse solution comprising a complexation reagent comprises a solution of thiourea and one or more of hydrochloric acid, nitric acid, sulfuric acid.

7. The method of any preceding embodiment, wherein the rinse solution comprising a complexation reagent comprises a solution of sodium thiosulfate and one or more of sodium bicarbonate, sodium carbonate, $\text{Ca}(\text{OH})_2$.
8. The method of any preceding embodiment, wherein the contaminants comprise transition metals.
9. The method of any preceding embodiment, wherein the transition metals comprise late transition metals.
10. The method of any preceding embodiment, wherein the transition metals comprise Ag, Pb, Sn, Zn, Al, Pd, Pt, Fe, Cu, Co, Ni, Al, or a combination thereof.
11. The method of any preceding embodiment, further comprising washing the refined precious metal with an aqueous solution.
12. The method of any preceding embodiment, further comprising pre-rinsing the precious metal prior to contacting with the refining solution, the pre-rinsing comprising contacting the precious metal with a dilute acidic solution; contacting the acid-washed precious metal with an aqueous solution; and contacting the aqueous-washed precious metal with a concentrated acid.
13. The method of any preceding embodiment, wherein the dilute acidic solution comprises HCl, HBr, HI, HNO_3 , H_2SO_4 , H_3PO_4 , or a combination thereof.
14. The method of any preceding embodiment, wherein the concentrated acid comprises glacial acetic acid.
15. The method of any preceding embodiment, wherein contacting the precious metal with the refining solution further comprises dosing the refining solution with additional oxidant.
16. The method of any preceding embodiment, wherein contacting the precious metal with the refining solution further comprises dosing the refining solution with additional oxidant at least once, or at least twice after contacting the precious metal with the refining solution.
17. The method of any preceding embodiment, wherein the acid of the refining solution comprises HCl, HBr, HI, chlorous acid, chloric acid, bromous acid, bromic acid, iodic acid, perchloric acid, sulfuric acid, nitric acid, oxalic acid, phosphoric acid, an organic acid, or combinations thereof.
18. The method of any preceding embodiment, wherein the acid of the refining solution comprises HCl, HBr, HI.
19. The method of any preceding embodiment, wherein the acid of the refining solution comprises HCl.

20. The method of any preceding embodiment, wherein the oxidant of the refining solution comprises HNO_3 , H_2O_2 , O_2 , bubbled air, I_2 , NaClO_2 , NaClO_3 , KClO_3 , NH_4ClO_3 , NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , $\text{Ca}(\text{ClO})_2$, Cl_2 , CuCl_2 , FeCl_3 , CaO_2 , sodium iodate, potassium iodate, manganese dioxide, perchloric acid, or combinations thereof.
- 5 21. The method of any preceding embodiment, wherein the oxidant of the refining solution comprises KClO_3 , NH_4ClO_3 , NaClO_3 .
22. The method of any preceding embodiment, wherein the oxidant of the refining solution comprises NaClO_3 .
23. The method of any preceding embodiment, wherein the ligand source of the refining
10 solution comprises a chloride salt.
24. The method of any preceding embodiment, wherein the ligand source of the refining solution comprises HCl , MgCl_2 , AlCl_3 , CaCl_2 , or a combination thereof.
25. The method of any preceding embodiment, wherein the ligand source of the refining solution comprises MgCl_2 .
- 15 26. The method of any preceding embodiment, wherein the partially water-miscible or water-miscible organic solvent of the refining solution comprises glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, or a combination thereof.
27. The method of any preceding embodiment, wherein the water-miscible organic solvent of the refining solution comprises glacial acetic acid, acetic acid, or a combination thereof.
- 20 28. The method of any preceding embodiment, wherein the water-miscible organic solvent of the refining solution comprises glacial acetic acid.
29. The method of any preceding embodiment, wherein the precious metal comprises Au, Pt, Pd, Rh, Ru, Ir, Os, or a combination thereof.
30. The method of any preceding embodiment, wherein the precious metal comprises Au,
25 Pd, Pt, Rh, or a combination thereof.
31. The method of any preceding embodiment, wherein the precious metal comprises Au.
32. The method of any preceding embodiment, wherein the refined precious metal has a purity of $\geq 99\%$, or $\geq 99.9\%$.
- 30 **[0012]** In one or more embodiments of the present disclosure, there is also provided:
1. A method of refining a precious metal, the method comprising: forming a refining solution, the refining solution comprising an acid in a partially water-miscible or water-miscible solvent; adding a precious metal to the refining solution; dosing an oxidant into the refining

solution; leaching the precious metal into the refining solution; and forming a leached solution comprising leached precious metal.

2. The method of embodiment 1, wherein dosing an oxidant into the refining solution comprises: continuously dosing the oxidant into the refining solution over a period of time;
5 and/or dosing the oxidant at time intervals.

3. The method of any one or more preceding embodiments, wherein continuously dosing the oxidant into the refining solution over a period of time comprises: dosing the oxidant into the refining solution for the duration of leaching the precious metal into the refining solution; or dosing the oxidant into the refining solution for a period of time that is less than the duration of
10 leaching the precious metal into the refining solution.

4. The method of any one or more preceding embodiments, wherein dosing the oxidant at time intervals comprises: adding a first dose of the oxidant to the refining solution when forming the refining mixture; and adding subsequent doses of the oxidant to the refining solution at intervals of time after adding the first dose.

15 5. The method of any one or more preceding embodiments, wherein adding subsequent doses of the oxidant comprise adding two or more additional doses of oxidant.

6. The method of any one or more preceding embodiments, wherein each of the intervals of time after adding the first dose is about 1 min to about 5 min; or about 1 min to about 4 min; or about 1 min to about 3 min; or about 1 min to 2 min; or about 1 min.

20 7. The method of any one or more preceding embodiments, further comprising filtering the leached solution to remove undissolved solids, precipitated solids, or a combination thereof.

8. The method of any one or more preceding embodiments, further comprising adding a reductant to the leached solution; and reducing the leached precious metal; and precipitating
25 reduced precious metal.

9. The method of any one or more preceding embodiments, wherein adding a reductant to the leached solution further comprises adding a first dose of a base to the leached solution a first period of time after adding the reductant; and optionally adding a second dose of the base a second period of time after adding the first dose of base.

30 10. The method of any one or more preceding embodiments, wherein the first period of time and/or the second period of time is about 1 to about 10 min; or about 3 to about 10 min; or about 7 to about 10 min.

11. The method of any one or more preceding embodiments, wherein the reductant comprises thiourea, sodium metabisulfite, sodium sulfite, or a combination.
12. The method of any one or more preceding embodiments, wherein the reductant comprises an aqueous solution of thiourea.
- 5 13. The method of any one or more preceding embodiments, wherein adding a reductant to the leached solution and reducing the leached precious metal comprises heating the leached solution.
14. The method of any one or more preceding embodiments, wherein heating the leached solution comprises bring the leached solution to a temperature above ambient temperature and below the boiling point of the leached solution.
- 10 15. The method of any one or more preceding embodiments, wherein heating the leached solution comprises bringing the leached solution to a temperature of about 35°C to about 75°C; or about 40°C to about 70°C; or about 45°C to about 65°C; or about 50°C to about 65°C; or about 55°C to about 65°C; or about 60°C.
- 15 16. The method of any one or more preceding embodiments, further comprising separating the reduced precious metal from the leached solution.
17. The method of any one or more preceding embodiments, further comprising washing the reduced precious metal with water, an aqueous solution, or a combination thereof.
18. The method of any one or more preceding embodiments, further comprising rinsing the reduced precious metal with a rinse solution to form a refined precious metal.
- 20 19. The method of any one or more preceding embodiments, wherein the rinse solution comprises a rinse acid, a rinse complexing agent, or a combination thereof.
20. The method of any one or more preceding embodiments, wherein the rinse solution comprises a rinse acid and a rinse complexing agent.
- 25 21. The method of any one or more preceding embodiments, wherein the rinse acid comprises acetic acid, glacial acetic acid, hydrochloric acid, nitric acid, sulfuric acid, or a combination thereof.
22. The method of any one or more preceding embodiments, wherein the rinse complexing agent comprises a thiourea, a thiosulfate, or a combination.
- 30 23. The method of any one or more preceding embodiments, wherein the rinse solution comprises an aqueous solution of thiourea and hydrochloric acid.
24. The method of any one or more preceding embodiments, wherein rinsing the reduced precious metal with a rinse solution comprises heating the rinse solution.

25. The method of any one or more preceding embodiments, wherein heating the rinse solution comprises bringing the rinse solution to a temperature above ambient temperature and below the boiling point of the rinse solution.
26. The method of any one or more preceding embodiments, wherein heating the rinse
5 solution comprises bring the rinse solution to a temperature of about 35°C to about 75°C; or about 40°C to about 70°C; or about 45°C to about 65°C; or about 50°C to about 65°C; or about 50°C to about 60°C; or about 60°C.
27. The method of any one or more preceding embodiments, further comprising washing the refined precious metal with water, an aqueous solution, or a combination thereof.
- 10 28. The method of any one or more preceding embodiments, wherein forming the refining solution, adding the precious metal to the refining solution, and dosing the oxidant into the refining solution comprises: combining the acid, a first dose of the oxidant, and a ligand source in the partially water-miscible or water-miscible solvent; and then adding the precious metal.
29. The method of any one or more preceding embodiments, wherein the ligand source
15 comprises a chloride salt.
30. The method of any one or more preceding embodiments, wherein the ligand source comprises MgCl_2 , AlCl_3 , CaCl_2 , or a combination thereof.
31. The method of any one or more preceding embodiments, further comprising recharging the refining solution with a final dose of the oxidant and a second dose of the acid.
- 20 32. The method of any one or more preceding embodiments, further comprising adding a second oxidant and a polyatomic salt to the leached solution to precipitate contaminants from the leached solution.
33. The method of any one or more preceding embodiments, wherein the polyatomic salt comprises an ammonium salt.
- 25 34. The method of any one or more preceding embodiments, wherein the polyatomic salt comprises ammonium chloride, ammonium sulfate, ammonium nitrate, or combinations thereof.
35. The method of any one or more preceding embodiments, wherein the second oxidant comprises HNO_3 , H_2O_2 , O_2 , bubbled air, I_2 , NaClO_2 , NaClO_3 , KClO_3 , NH_4ClO_3 , NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$,
30 KMnO_4 , $\text{Ca}(\text{ClO})_2$, Cl_2 , CuCl_2 , FeCl_3 , CaO_2 , sodium iodate, potassium iodate, manganese dioxide, perchloric acid, or combinations thereof.
36. The method of any one or more preceding embodiments, wherein the second oxidant comprises KClO_3 , NH_4ClO_3 , NaClO_3 .

37. The method of any one or more preceding embodiments, wherein the second oxidant comprises NaClO_3 .
38. The method of any one or more preceding embodiments, further comprising pre-rising the precious metal before adding the precious metal to the refining solution.
- 5 39. The method of any one or more preceding embodiments, wherein pre-rinsing the precious metal comprises rinsing the precious metal with the partially water-miscible or water-miscible solvent; acetic acid, glacial acetic acid, or a combination thereof; water, an aqueous solution, or a combination thereof; and/or the rinse solution of any one or more preceding embodiments.
- 10 40. The method of any one or more preceding embodiments, wherein the acid of the refining solution comprises HCl , HBr , HI , chlorous acid, chloric acid, bromous acid, bromic acid, iodic acid, iodic acid, perchloric acid, sulfuric acid, nitric acid, oxalic acid, phosphoric acid, methanesulfonic acid, citric acid, an organic acid, or combinations thereof.
- 15 41. The method of any one or more preceding embodiments, wherein the acid of the refining solution comprises HCl , HBr , HI .
42. The method of any one or more preceding embodiments, wherein the acid of the refining solution comprises HCl .
43. The method of any one or more preceding embodiments, wherein the oxidant of the refining solution comprises HNO_3 , H_2O_2 , O_2 , bubbled air, I_2 , NaClO_2 , NaClO_3 , KClO_3 , NH_4ClO_3 ,
20 NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , $\text{Ca}(\text{ClO})_2$, Cl_2 , CuCl_2 , FeCl_3 , CaO_2 , sodium iodate, potassium iodate, manganese dioxide, perchloric acid, or combinations thereof.
44. The method of any one or more preceding embodiments, wherein the oxidant comprises KClO_3 , NH_4ClO_3 , NaClO_3 .
45. The method of any one or more preceding embodiments, wherein the oxidant
25 comprises NaClO_3 .
46. The method of any one or more preceding embodiments, wherein the partially water-miscible or water-miscible solvent comprises glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, or a combination thereof.
47. The method of any one or more preceding embodiments, wherein the partially water-
30 miscible or water-miscible solvent comprises aqueous solutions of glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, or a combination thereof.

48. The method of any one or more preceding embodiments, wherein the partially water-miscible or water-miscible solvent comprises: glacial acetic acid; acetic acid; an aqueous solution of glacial acetic acid; and aqueous solution of acetic acid; or a combination thereof.
49. The method of any one or more preceding embodiments, wherein the partially water-miscible or water-miscible solvent comprises glacial acetic acid; an aqueous solution of glacial acetic acid; or a combination thereof.
50. The method of any one or more preceding embodiments, wherein the aqueous solution of glacial acetic acid comprises about 20% by volume to about 30% by volume glacial acetic acid.
51. The method of any one or more preceding embodiments, wherein the precious metal comprises Au, Pt, Pd, Rh, Ru, Ir, Os, or a combination thereof.
52. The method of any one or more preceding embodiments, wherein the precious metal comprises Au, Pd, Pt, Rh, or a combination thereof.
53. The method of any one or more preceding embodiments, wherein the precious metal comprises Au.
54. The method of any one or more preceding embodiments, wherein the refined precious metal has a purity of $\geq 99\%$, $\geq 99.9\%$, or $\geq 99.99\%$.
55. A system for refining a precious metal, the system comprising: a leach reactor, the leach reactor having a first agitator and a first port for dosing a precious metal into the leach reactor, the leach reactor being in fluid communication with a leach dosing system for dosing a refining solution into the leach reactor; and a reduction reactor in fluid communication with the leach reactor, the reduction reactor having a second agitator, and being in fluid communication with a reducing dosing system for dosing a reducing mixture into the reduction reactor, and a rinsing system for dosing a rinse solution into the reduction reactor; the precious metal and refining solution being dosed into the leach reactor and agitated to leach the precious metal into the refining solution and form a leached solution comprising a leached precious metal; the leached solution being transferred to the reduction reactor; the reducing mixture being dosed into the reduction reactor; and being agitated to reduce the precious metal and form precipitated precious metal.
56. The system of embodiment 55, further comprising a first polishing filter system in fluid communication with the leach reactor, the first polishing filter system comprising a filter in fluid communication with the leach reactor and a first transfer pump, the transfer pump being in fluid

communication with the reduction reactor; wherein: the leached solution being transferred to the reduction reactor comprises filtering the leached solution through the polishing filter system to remove insoluble impurities from the leached solution.

57. The system of any one or more preceding embodiments, further comprising a first polishing filter system coupled to leach reactor, the first polishing filter system comprising a filter system coupled to the leach reactor and a first transfer pump, the transfer pump being in fluid communication with the reduction reactor; wherein: the leached solution being transferred to the reduction reactor comprises filtering the leached solution through the polishing filter system to remove insoluble impurities from the leached solution.

58. The system of any one or more preceding embodiments, further comprising a second polishing filter system coupled to the reduction reactor, the second polishing filter system comprising a filter system coupled to the reduction reactor in fluid communication with a second transfer pump, the transfer pump being in fluid communication with the reduction reactor; wherein reducing the precious metal and forming precipitated precious metal comprises forming a spent leached solution and precipitated precious metal mixture, and filtering the mixture through the second polishing filter system to remove the precipitated precious metal from the mixture.

59. The system of any one or more preceding embodiments, further comprising a second polishing filter in fluid communication with the reduction reactor, the second polishing filter system comprising a filter in fluid communication with reduction reactor and a second transfer pump, the transfer pump being in fluid communication with the reduction reactor; wherein reducing the precious metal and forming precipitated precious metal comprises forming a spent leached solution and precipitated precious metal mixture, and filtering the mixture through the second polishing filter system to remove the precipitated precious metal from the mixture.

60. The system of any one or more preceding embodiments, wherein filtering the mixture through the second polishing filter system to remove the precipitated precious metal from the mixture comprises recycling the filtered spent leached solution back to the reduction reactor.

61. The system of any one or more preceding embodiments, wherein filter system comprises a base to couple to the reactor; a filter medium coupled to the base.

62. The system of any one or more preceding embodiments, wherein the filter medium comprises a frit and/or optionally least one filter paper.

63. The system of any one or more preceding embodiments, wherein the frit and/or optionally least one filter paper comprises a polyalkylene, a polyfluorinated polymer, or a combination thereof.
64. The system of any one or more preceding embodiments, wherein the frit comprises a
5 about 1 micron to about 5 micron rating.
65. The system of any one or more preceding embodiments, wherein the at least one filter paper comprises a about 0.45 to about 3 micron rating.
66. The system of any one or more preceding embodiments, wherein the leach dosing system comprises a first reagent drum in fluid communication with a first reagent pump, the
10 first reagent drum comprising the refining solution and the first reagent pump in fluid communication with the leach reactor.
67. The system of any one or more preceding embodiments, wherein the refining solution comprises a solvent, an acid, and an oxidant, and the leach dosing system comprises: a leach solvent drum in fluid communication with a leach solvent pump, the leach solvent pump being
15 in fluid communication with the leach reactor; a leach acid drum in fluid communication with a leach acid pump, the leach acid pump being in fluid communication with the leach reactor; and a leach oxidant drum in fluid communication with a leach oxidant pump, the leach oxidant pump being in fluid communication with the leach reactor; wherein: the solvent, acid, and oxidant are separately dosed into the leach reactor to form the refining in the leach reactor.
- 20 68. The system of any one or more preceding embodiments, wherein the reducing dosing system comprises a second reagent drum in fluid communication with a second reagent pump, the second reagent drum comprising the reducing mixture and the second pump being in fluid communication with the reduction reactor.
69. The system of any one or more preceding embodiments, wherein the reducing mixture
25 comprises a reductant, optionally in solution, and the reducing dosing system comprises: a reagent make-up reactor, the reagent make-up reactor having an agitator and a first port for dosing the reductant into the mixing reactor, the reagent make-up reactor being in fluid communication with the reduction reactor; and an optional solution drum in fluid communication with an optional solution pump, the solution pump being in fluid communication
30 with the reagent make-up reactor; wherein: the reductant and optional solution are dosed into the reagent make-up reactor and agitated to form the reducing mixture.
70. The system of any one or more preceding embodiments, wherein the reducing mixture comprises a reductant in solution, and the system comprises the solution drum and pump.

71. The system of any one or more preceding embodiments, wherein the reducing mixture comprises a reductant in aqueous solution, and the solution drum and pump as an aqueous solution drum and an aqueous solution pump.

72. The system of any one or more preceding embodiments, wherein the rinse solution
5 comprises a rinse acid and a rinse complexing agent, and the rinsing system comprises: a third reagent drum in fluid communication with a third reagent pump, the third reagent drum comprising a rinse acid and the third pump being in fluid communication with the reduction reactor; and a fourth reagent drum in fluid communication with a fourth reagent pump, the
10 fourth reagent drum comprising a rinse complexing agent and the fourth pump being in fluid communication with the reduction reactor; wherein: rinse complexing agent and rinse acid are dosed into the reduction reactor to form the rinse solution, and the rinse solution is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal.

73. The system of any one or more preceding embodiments, wherein the fourth reagent
15 drum in fluid communication with the fourth reagent pump, the fourth reagent drum comprising a rinse complexing agent and the forth pump being in fluid communication with the reducing reactor comprises the reducing dosing system, wherein the solution drum and pump are an aqueous solution drum and an aqueous solution pump, and aqueous solution is dosed into the reduction reactor, the reductant is dosed into the reduction reactor, and the rinse acid is dosed
20 into the reduction reactor, to form the rinse solution, and the rinse solution is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal.

74. The system of any one or more preceding embodiments, further comprising dosing additional aqueous solution into the reduction reactor and flowing through the precipitated
25 precious metal collected within the second polishing filter system to rinse the precipitated precious metal.

75. The system of any one or more preceding embodiments, wherein the third reagent drum in fluid communication with the third reagent pump, the third reagent drum comprising the rinse acid and the third pump being in fluid communication with the reduction reactor
30 comprises the leach acid drum in fluid communication with a leach acid pump, the leach acid pump being diverted to be in fluid communication with the reduction reactor.

76. The system of any one or more preceding embodiments, wherein the rinse solution comprises a rinse acid and a rinse complexing agent, the rinse complexing agent comprising

the reducing mixture, and the rinsing system comprises: a third reagent drum in fluid communication with a third reagent pump, the third reagent drum comprising the rinse acid and the third pump being in fluid communication with the reduction reactor; a fourth reagent drum in fluid communication with a fourth reagent pump, the fourth reagent drum comprising an aqueous solution and the forth pump being in fluid communication with the reducing reactor; and the reducing dosing system; wherein: the aqueous solution is dosed into the reduction reactor, the reducing mixture is dosed into the reduction reactor, and the rinse acid is dosed into the reduction reactor, to form the rinse solution, and the rinse solution is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal; and optionally an additional dose of aqueous solution is dosed into the reduction reactor and is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal.

BRIEF DESCRIPTION OF THE FIGURES

[0013] Embodiments of the present disclosure will now be described, by way of example only, with reference to the attached Figures.

[0014] FIG. 1 depicts a schematic of a refining system as described herein.

[0015] FIG. 2 depicts an exploded view of a filter system as described herein.

[0016] FIG. 3 depicts A. A photo showing thiourea reduction of gold at (left to right) room temperature, 60°C, 45°C, and in an ice bath, after 20 minutes of reaction. B. A photo showing thiourea reduction of gold at (left to right) room temperature, 60°C, 45°C, and in an ice bath, after 40 minutes of reaction. C. A photo showing thiourea reduction of gold at (left to right) room temperature, 60°C, 45°C, and in an ice bath, after 60 minutes of reaction. D. A photo showing thiourea reduction of gold at (left to right) room temperature, 60°C, 45°C, and in an ice bath, after 60 minutes of reaction.

[0017] FIG 4. depicts a cross-sectional view of a leach reactor, before (A) and after (B) modification to reduce or avoid precious metal build up.

DETAILED DESCRIPTION

[0018] Unless defined otherwise, all technical and scientific terms used herein have the meaning as commonly understood in the art.

[0019] As used in the specification and claims, the singular forms "a", "an" and "the" include plural references unless the context dictates otherwise.

[0020] The term “comprising” and its derivatives, as used herein, refer to the presence of the stated features, elements, components, groups, integers, and/or steps, etc., but do not exclude the presence of other unstated features, elements, components, groups, integers and/or steps, etc. The foregoing also applies to words having similar meanings such as the terms, “including”, “having” and their derivatives. The term “consisting” and its derivatives, as used herein, refer to the presence of the stated features, elements, components, groups, integers, and/or steps, etc., but exclude the presence of other unstated features, elements, components, groups, integers and/or steps, etc. The term “consisting essentially of”, as used herein, refers to the presence of the stated features, elements, components, groups, integers, and/or steps, etc. as well as those that do not materially affect the characteristic(s) of features, elements, components, groups, integers, and/or steps, etc.

[0021] The term “precious metal” or “precious metals” as used herein refers to gold and/or platinum group metals, such as platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os). In one or more embodiments, “precious metal” refers to gold, palladium, and/or platinum. In one or more embodiments, “precious metal” refers to gold. In yet other embodiments, “precious metal” refers to palladium, rhodium, and/or platinum.

[0022] The term “base metal” or “base metals” as used herein refers to any nonferrous metals that are neither precious metals nor noble metals; for example: copper, lead, nickel, tin, aluminum, and zinc.

[0023] The term “ferrous metal” or “ferrous metals” refers to metals and alloys comprising iron; for example: steel, alloy steel, carbon steel, cast iron, and wrought iron.

[0024] The term “ambient pressure” refers to the pressure of the surrounding medium, such as a gas or liquid, in contact with an object(s). The term “ambient temperature” refers to the temperature of the air (or other medium and surroundings) in any particular place, as measured by a thermometer. As used herein, “room temperature” generally refers to a temperature in a range of about 20 °C to about 25 °C; or may be used interchangeably with “ambient temperature”.

[0025] The term “miscible” as used herein when referring to two liquid phases means that the two liquid phases can, for example be mixed in all proportions to form a homogeneous solution. Two miscible liquid phases will not, for example separate into two liquid phases after mixing. Accordingly, a “water-miscible” liquid such as a “water-miscible organic solvent” or a “water-miscible solvent” is a liquid that can be mixed with water to form a homogeneous solution.

[0026] The term “partially miscible” as used herein when referring to two liquid phases means that the two liquid phases will, for example, separate into two liquid phases after mixing, each liquid phase containing a portion of the other liquid phase in a dissolved state. Accordingly, a “partially water-miscible organic solvent” or “partially water-miscible solvent” is a liquid that, after mixing with water, will separate into two liquid phases after mixing, one phase being water containing a portion, for example, about 10% (v/v) of the partially water-miscible organic liquid in a dissolved state, and the other phase being the partially water-miscible organic liquid containing a portion, for example, about 10% (v/v) of water in a dissolved state.

[0027] The term “and/or” as used herein means that the listed items are present, or used, individually or in any combination (e.g., A, B,... X, **and/or** Y” refers to “A, B,... X, **and** Y”; or “one of A, B,... X, **or** Y”; or any combination of A, B,... X, Y). In effect, this term means that “at least one of” or “one or more” of the listed items is used or present.

[0028] Terms of degree such as “substantially”, “about” and “approximately” as used herein refer to a reasonable amount of deviation of the modified term such that the end result is not significantly changed. In one or more embodiments, these terms of degree refer to a deviation of at least $\pm 5\%$ of the modified term if this deviation would not negate the meaning of the word it modifies.

[0029] In embodiments comprising an “additional” or “second” component, such as an additional or second compound, the additional or second component as used herein is chemically different from the other components or first component. A “third” component is different from the other, first, and second components, and further enumerated or “additional” components are similarly different.

[0030] The term “suitable” as used herein refers to the selection of specific reagents or conditions depending on the reaction being performed and the desired results, but none-the-less, can generally be made by a person skilled in the art once all relevant information is known and/or considered.

[0031] The terms “refining solution”, “leaching solution”, “leaching mixture”, leach solution”, “leach mixture”, “lixiviant” and “lixiviant solution” are used interchangeably herein, unless context indicates otherwise..

[0032] The term “drum” as used herein refers to a container. The container may be any container suitable for containing liquids, solids, and/or gases. The container may be any

container suitable for containing liquids, solids, and/or gases; and configured to communicate with the systems as described herein.

[0033] Precious Metal Refining

5 **[0034]** Refining is a process by which impurities can be removed from a substance, such as a precious metal. For example, when said precious metal is gold, refining gold can result in gold with a purity of $\geq 99\%$, $\geq 99.9\%$, about 99.99% , or $\geq 99.99\%$. Gold having a purity of 99.99% is also known as fine gold or 9999. In 9999 gold, it is expected to see less than 100 mg/kg of impurities.

10 **[0035]** Refining a precious metal such as gold present several challenges due to the metal's inherent properties - including its inert nature, high density, and exceptional resistance to corrosion. These characteristics make a precious metal such as gold difficult to chemically react under standard conditions, requiring extreme measures - such as high temperatures, or utilizing toxic reagents. Its high density complicates handling and separation processes, as the
15 precious metal can settle quickly, making uniform mixing and processing more challenging. Furthermore, its resistance to corrosion necessitates the use of specialized and durable materials for refining equipment, thereby increasing costs and technical demands, particularly when aiming for ultra-high purity levels such $99.99\% +$.

[0036] The Miller process is a dominant industrial method for refining precious metals
20 such as gold, primarily because of its efficiency in producing gold with 99.9% purity. This process involves melting gold and introducing chlorine gas, which reacts with impurities to form chlorides that can be separated from the molten gold. However, the Miller process has several drawbacks. It is highly energy-intensive due to the need to melt gold, and the use of toxic chlorine gas requires stringent safety protocols to protect workers and the environment. While
25 effective for large-scale operations, the Miller process must often be paired with the Wohlwill process to achieve ultra-high purities, such as 99.99% or higher, adding to its complexity and cost.

[0037] The Wohlwill process is a complementary method that can refine a precious
30 metal such as gold to the high levels of purity. This electrolytic process requires precise control over current and chemical composition of a chloroauric acid leach solution to avoid contamination during refinement. A significant drawback is the necessity of using a gold bar as the anode, which locks up a substantial amount of capital in the process. Furthermore, the Wohlwill process demands skilled operators and meticulous monitoring, increasing operational

complexity. Equipment maintenance is also crucial due to the corrosive nature of the chloroauric acid solution, which further adds to costs.

[0038] An alternative industrial method is the aqua regia process, which dissolves precious metals such as gold using a mixture of concentrated nitric acid and hydrochloric acid.

5 While effective, this method has its own set of challenges. The process relies on highly toxic and corrosive chemicals, requiring stringent safety measures and careful waste management to prevent environmental contamination. Impurity control is another significant challenge, as coprecipitation during the process' precipitation phase can make it difficult to achieve consistent purity. Additionally, the volatility of the solution and the generation of hazardous
10 byproducts make this method less suitable for large-scale operations. Furthermore, achieving 99.99% purity is typically not feasible with aqua regia and so it also requires the Wohlwill process to attain this level of refinement.

[0039] Described herein is a method of refining a precious metal (otherwise referred to herein as a refining method), which may avoid one or more of the challenges delineated above,
15 while providing a refined precious metal having a purity of $\geq 99\%$ (99+), $\geq 99.9\%$ (999+), about 99.99% (9999), or $\geq 99.99\%$ (9999+).

[0040] Refining Solution

[0041] The refining method described herein involves use of a refining solution, where that refining solution solubilizes - otherwise referred to herein as dissolves, or leaches - a
20 precious metal to be refined. The refining solution comprises an acid and a partially water-miscible or water-miscible solvent. The refining solution further comprises an oxidant, which may be separately dosed into the refining solution continuously, or at set time intervals during the solubilization, or leaching of the precious metal. The refining solution optionally further comprises a ligand source, which may interact with leached precious metal to form a stabilizing
25 metal-ligand complex that may facilitate leaching.

[0042] Acid of Refining Solution

[0043] The acid of the refining solution may be any proton donor suitable for the precious metal being refined. A suitable acid may be selected in view of (i) the original purity of the precious
30 metal; (i) the desired purity of the refined precious metal; (iii) the material from which the precious metal is sourced; and/or (iv) what is other metals, salts, compounds, components, etc. may be present in said material.

- [0044] For example, where a 999+ or 9999+ purity is desired for a refined precious metal, an acid may be selected that will not introduce its own contaminants into the refining method (by-products of its synthesis, its counter ion(s), etc.). Where the material from which the precious metal is to be leached is difficult to process, in terms resistance to physical or chemical breakdown, an acid may be selected that is strong enough (that is, has a low enough pK_a) to suitably leach or dissolve the precious metal from the material. Where one acid may react with (i) components or chemicals used during the refining method; (ii) the precious metal or material from which the precious metal is sourced; etc. to form noxious or toxic by-products (for example, NO_x gas being formed from HNO_3), then another acid may be selected that will not form such by-products.
- 5 [0045] The acid may be a suitably strong acid. The acid may have a pK_a of <3 , or <2.5 , or <2 , or <1 , or <0 . The acid may act as a ligand source, as described below. In one or more embodiments where the acid acts as a ligand source, as described below, an additional ligand source need not be added to the refining solution. The acid may have oxidizing properties, and thus may facilitate oxidizing the precious metal along with the oxidant described below. In one or
- 15 more embodiments where the acid has oxidizing properties, a separate oxidant may nonetheless be added such that the acid and the oxidant are not the same compound. The acid may comprise HCl, HBr, HI, chlorous acid, chloric acid, bromous acid, bromic acid, iodic acid, perchloric acid, sulfuric acid, nitric acid, oxalic acid, phosphoric acid, methanesulfonic acid, citric acid, an organic acid, or combinations thereof. The acid may comprise HCl, HBr, HI, or
- 20 combinations thereof. The acid of the refining solution may comprise HCl.
- [0046] The concentration of the acid is measured in the partially water-miscible or water-miscible solvent of the refining solution. The acid may be present in any concentration suitable for leaching a precious metal. The acid may have a concentration in the partially water-miscible or water-miscible solvent of about 0.01 M to about 10 M; or has any concentration or
- 25 any range of concentrations within about 0.01 M and about 10 M. The acid may have a concentration in the in the partially water-miscible or water-miscible solvent of about 0.01 M to about 10 M; or about 0.01 M to about 8 M; or about 0.01 M to about 6 M; or about 0.01 M to about 4 M.
- [0047] Oxidant of Refining Solution
- 30 [0048] The oxidant of the refining solution may be any oxidant suitable for the precious metal being refined. A suitable oxidant may be selected in view of (i) the original purity of the precious metal; (ii) the desired purity of the refined precious metal; (iii) the material from which the

precious metal is sourced; and/or (iv) what is other metals, salts, compounds, components, etc. may be present in said material.

[0049] As noted above, where a 999+ or 9999+ purity is desired for a refined precious metal, an oxidant may be a selected that will not introduce its own contaminants into the refining method (by-products of its synthesis, its counter ion(s), etc.). Where the material from which the precious metal is to be leached is difficult to process, in terms resistance to physical or chemical breakdown, an oxidant may be selected that is strong enough (that is, has a high enough redox potential) to suitably facilitate leaching and/or oxidizing the precious metal from the material. Where one oxidant may react with (i) components or chemicals used during the refining method; (ii) the precious metal or material from which the precious metal is sourced; etc. to form noxious or toxic by-products (for example, Cl_2 gas being formed from reaction of oxidant with acid), then another oxidant may be selected that will not form such by- products.

[0050] The oxidant may be an oxidant that is suitably strong enough to oxidize the precious metal in the presence of the other components of the refining solution, such as the acid, optional ligand source, etc. The oxidant may have acidic properties, and thus may facilitate leaching the precious metal along with the acid described above. In one or more embodiments where the oxidant has acidic properties, a separate acid may nonetheless be added such that the acid and the oxidant are not the same compound. The oxidant may comprise HNO_3 , H_2O_2 , O_2 , bubbled air, I_2 , NaClO_2 , NaClO_3 , KClO_3 , NH_4ClO_3 , NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , $\text{Ca}(\text{ClO})_2$, Cl_2 , CuCl_2 , FeCl_3 , CaO_2 , sodium iodate, potassium iodate, manganese dioxide, perchloric acid, or combinations thereof. The oxidant may comprise KClO_3 , NH_4ClO_3 , NaClO_3 , NaClO , or combinations thereof. The oxidant may comprise NaClO_3 .

[0051] The concentration of the oxidant is measured in the partially water-miscible or water-miscible solvent of the refining solution. The concentration of the oxidant may be present in any concentration suitable to facilitate leaching and/or oxidization of the precious metal. The oxidant may have a concentration in the partially water-miscible or water-miscible solvent of about 0.01 M to about 5 M; or has any concentration or any range of concentrations within about 0.01 M and about 5 M. The oxidant may have a concentration in the in the partially water-miscible or water-miscible solvent of about 0.01 M to about 5 M; or about 0.01 M to about 4 M; or about 0.01 M to about 3 M; or about 0.01 M to about 2.5 M.

[0052] The oxidant may be added to the refining solution along with the acid. The oxidant may be added to the refining solution along with the acid and/or precious metal. The

oxidant may be dosed into the refining solution after the acid and/or precious metal are added to the refining solution.

[0053] When the oxidant is dosed into the refining solution, it may be continuously dosed into the refining solution over a period of time. For example, the oxidant may be continuously dosed into the refining solution for the duration of leaching the precious metal into the refining solution. The oxidant may be continuously dosed into the refining solution for a period of about 1 min to about 10 min, or for a period of time of about 5 min. The period of time may be selected based on the amount of precious metal to be dissolved, and may be modified should undissolved precious metal remain after the initial period of time.

[0054] When the oxidant is dosed into the refining solution, it may be discretely dosed at specific time intervals. For example, after an initial dose of oxidant is added to the refining solution, additional oxidant may be added at 1 min intervals, 3 min intervals, 5 min intervals, 8 min intervals, 10 min intervals, etc. After the initial dose, the oxidant may be dosed into the refining solution 1 more time, 2 more times, 3 more time, 4 more times, etc. The number of oxidant doses and length of each time interval may be selected based on the amount of precious metal to be dissolved, the desired rate of leaching precious metal into the refining solution, etc. and may be modified should undissolved precious metal persist.

[0055] Ligand Source of Refining Solution

[0056] The ligand source of the refining solution may be any ligand source suitable for the precious metal being leached into the refining solution, as described herein. The ligand of the ligand source may interact with precious metal into the refining mixture to form a precious metal-ligand complex. Without wishing to be bound by theory, formation of the metal-ligand complex may stabilize the dissolved precious metal in solution, which may facilitate leaching the precious metal into the refining solution.

[0057] A suitable ligand source may be selected in view of (i) the original purity of the precious metal; (i) the desired purity of the refined precious metal; (iii) the material from which the precious metal is sourced; and/or (iv) what is other metals, salts, compounds, components, etc. may be present in said material. As noted above, where a 999+ or 9999+ purity is desired for a refined precious metal, a ligand may be a selected that will not introduce its own contaminants into the refining method (by-products of its synthesis, its counter ion(s), etc.). Where the material from which the precious metal is to be leached is difficult to process, in terms resistance to physical or chemical breakdown, a ligand source may be selected that has a high affinity for forming metal

complexes with the precious metal being leached that it facilitates leaching the precious metal from the material. Where one ligand source may react with (i) components or chemicals used during the refining method; (ii) the precious metal or material from which the precious metal is sourced; etc. to form unwanted by-products (for example, an insoluble salt that precipitates out of the refining solution), then another ligand source may be selected that will not form such by-products.

[0058] The ligand source may be any source of Cl^- ligand. The ligand source may be a chloride salt. The ligand source may be an alkali metal chloride salt, and alkaline earth metal chloride salt, or a combination thereof. The ligand source may comprise NaCl , LiCl , MgCl_2 , AlCl_3 , CaCl_2 , or a combination thereof. The ligand source may comprise NaCl , MgCl_2 , CaCl_2 , or a combination thereof. The ligand source may comprise MgCl_2 .

[0059] The concentration of the ligand source is measured in the partially water-miscible or water-miscible solvent of the refining solution. The concentration of the ligand source may be present in any concentration suitable to facilitate leaching or solubilization of the precious metal. The ligand source may have a concentration in the partially water-miscible or water-miscible solvent of about 0.1 M to about 4 M, or about 0.1 M to about 3 M, or about 0.1 M to about 2 M, or about 0.1 M to about 1 M, or about 0.1 M to about 0.5 M, or about 0.1 to about 0.4 M, or about 0.1 M to about 0.3 M, or about 0.1 to about 0.2 M; or is at any concentration or any range of concentrations within about 0.1 M and about 4 M.

[0060] When a separate ligand source is not added to the refining solution, the acid of the refining solution may act as a ligand source.

[0061] Solvent of Refining Solution

[0062] The partially water-miscible or water-miscible solvent of the refining solution may be any partially water-miscible or water-miscible solvent suitable for the solubilization of the acid, oxidant, optional ligand source, and leached precious metal of the refining method described herein.

[0063] The solvent may comprise ethyl acetate, acetonitrile, tetrahydrofuran, acetic acid, glacial acetic acid, or combinations thereof; or the solvent may comprise any one, or any subset of the group comprising, consisting essentially of, or consisting of ethyl acetate, acetonitrile, tetrahydrofuran, acetic acid, glacial acetic acid, or combinations thereof. The solvent may comprise, consist essentially of, or consist of acetic acid. The solvent may comprise, consist essentially of, or consist of glacial acetic acid.

[0064] As used herein, a "solvent" refers to a liquid that makes up at least 50wt% of the liquid phase of the herein described refining solution. As such, the refining solution may comprise or contain up to, or greater than 10 wt% water - for example between 1 wt% to 30 wt% water - and the solvent of the refining solution remains the partially water-miscible or water-miscible solvent, as the water is not present in amounts greater than 50 wt%. If the solvent of the refining solution comprises water, the amount of water can be selected to maintain leaching rates, leaching efficiencies, and/o yield of leached precious metal, while keeping below 50 wt% water.

[0065] Further, in one or more embodiments where the solvent comprises acetic acid or glacial acetic acid, the solvent does not act as the acid of the refining mixture, as the pKa of acetic acid or glacial acetic acid is between about 4 and about 5 - and is not <3. Thus, in one or more embodiments where the solvent comprises acetic acid or glacial acetic acid, the solvent does not act as the acid, as it is not a strong enough acid.

[0066] Thus, the partially water-miscible or water-miscible solvent may comprise aqueous solutions of glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, or a combination thereof; or the solvent may comprise any one, or any subset of the group comprising, consisting essentially of, or consisting of aqueous solutions of glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, or a combination thereof. The solvent may comprise an aqueous solution of acetic acid; an aqueous solution of glacial acetic acid; or a combination thereof. The solvent may comprise an aqueous solution of glacial acetic acid, such that the refining solution comprises about 30% glacial acetic acid by volume. The solvent may comprise an aqueous solution of glacial acetic acid that comprises about 60% by volume to about 70% by volume glacial acetic acid, such that the refining solution comprises about 30% glacial acetic acid by volume. The solvent may comprise an aqueous solution of acetic acid, such that the refining solution comprises about 30% acetic acid by volume. The solvent may comprise an aqueous solution of acetic acid that comprises about 60% by volume to about 70% by volume acetic acid, such that the refining solution comprises about 30% glacial acetic acid by volume.

[0067] **Leached Solution**

[0068] The refining method described herein provides a leached solution. The leached solution is formed from leaching (otherwise referred to herein as solubilizing or dissolving) the precious metal into the refining solution. Once the leached solution is formed, it may then be further processed - as described herein - via a series of reduction steps, precipitation steps, filtration steps, and rinse steps to provide a refined precious metal.

[0069] Reduction Step

[0070] The refining method described herein further comprises adding a reductant to the leached solution to reduce the leached precious metal. The leached precious metal may reduce from a positive oxidation state to an oxidation state of zero. So reduced, the precious metal may precipitate from solution.

[0071] The reductant added to the leached solution may be any reductant suitable for reducing the precious metal being refined. A suitable reductant may be selected in view of (i) the original purity of the precious metal; (ii) the desired purity of the refined precious metal; (iii) the material from which the precious metal is sourced; and/or (iv) what other metals, salts, compounds, components, etc. may be present in said material. For example, where a 999+ or 9999+ purity is desired for a refined precious metal, a reductant may be selected that will not introduce its own contaminants into the refining method (by-products of its synthesis, its counter ion(s), etc.). A reductant that already comprises a metal may not be selected where that metal could interfere with the refining of the precious metal.

[0072] The reductant may comprise sodium metabisulfite, sodium sulfite, thiourea, sulfur dioxide, sodium sulfate, ascorbic acid, oxalic acid, hydrazine, hydrazine hydrochloride, hydroxylamine, hydroxylamine hydrochloride, or a combination thereof. The reductant may comprise sodium metabisulfite, sodium sulfite, thiourea, or a combination thereof. The reductant may comprise thiourea.

[0073] The reductant may comprise aqueous solutions of sodium metabisulfite, sodium sulfite, thiourea, sulfur dioxide, sodium sulfate, ascorbic acid, oxalic acid, hydrazine, hydrazine hydrochloride, hydroxylamine, hydroxylamine hydrochloride, or a combination thereof. The reductant may comprise aqueous solutions of sodium metabisulfite, sodium sulfite, thiourea, or a combination thereof. The reductant may comprise aqueous thiourea. The aqueous solutions may be saturated aqueous solutions.

[0074] If the precious metal and/or the material from which the precious metal is sourced comprises metal contaminants, a reductant may be selected that reduces the precious metal over, or instead of the metal contaminants so that those metal contaminants remain in solution. Various metal contaminants may be encountered, including Ag, Pb, Sn, Zn, Al, Pd, Pt, Fe, Cu, Co, Ni, Al, or a combination thereof. Metals such as Pd and/or Pt may only be considered contaminants in the context of wanting to purify other precious metals to 9999+ purity, such as gold.

[0075] Sodium metabisulfite may be selected as a reductant where the precious metal and/or material from which the precious metal is sourced comprises lower concentrations to no concentration of Pd, Sn, Pb, Ag, Cu, Fe, Zn, Ni, and/or Al - as sodium metabisulfite may reduce these metals along with the precious metal.

5 [0076] Sodium sulfite may be selected as a reductant where the precious metal and/or material from which the precious metal is sourced comprises lower concentrations to no concentration of Sn, Pb, Ag, Cu, Fe, and/or Ni - as sodium metabisulfite may reduce these metals along with the precious metal. Sodium sulfite may be selected as a reductant where the precious metal and/or material from which the precious metal is sourced comprises higher
10 concentrations of Pd, Zn and/or Al - as sodium metabisulfite may leave these metals in the leached solution and otherwise reduce the precious metal.

[0077] Thiourea be selected as a reductant where the precious metal and/or material from which the precious metal is sourced comprises lower concentrations to no concentration of Pb, Fe, and/or Ni - as thiourea may reduce these metals along with the precious metal.
15 Thiourea may be selected as a reductant where the precious metal and/or material from which the precious metal is sourced comprises higher concentrations of Pd, Ag, Cu, Zn, and/or Al - as thiourea may leave these metals in the leached solution and otherwise reduce the precious metal.

[0078] The concentration of the reductant may be present in any concentration suitable to facilitate reduction the precious metal. The reductant may have a concentration of about 0.01 M to about 5 M; or has any concentration or any range of concentrations within about 0.01 M and about 5 M. The reductant may have a concentration in the in the partially water-miscible or water-miscible solvent of about 0.01 M to about 5 M; or about 0.01 M to about 4 M; or about 0.01 M to about 3 M; or about 0.01 M to about 2.5 M.

25

[0079] Precipitation Step

[0080] As described above, the precious metal and/or the material from which the precious metal is sourced may comprise metal contaminants, which may include Pd and/or Pt. Such metals may only be considered contaminants in the context of wanting to purify other
30 precious metals to 9999+ purity, such as gold. Otherwise, Pd and/or Pt may be considered valuable metals.

[0081] To this end, the refining method described herein may further comprise a precipitation step when the precious metal and/or the material from which the precious metal is

sourced comprises platinum group metal contaminants, such as Pd and/or Pt. The precipitation step comprises adding a second oxidant and a polyatomic salt to the leached solution to precipitate the contaminants.

[0082] The second oxidant may be any oxidant suitable for oxidizing platinum group metals. The oxidant may comprise H_2O_2 , CaO_2 , Cl_2 , I_2 , HNO_3 , CaO_2 , MnO_2 , NaIO_3 , CuCl_2 , FeCl_3 , HClO_4 , NaClO_2 , NaClO_3 , NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , $\text{Ca}(\text{ClO})_2$, O_2 from air, or combinations thereof. The oxidant may comprise HNO_3 , H_2O_2 , O_2 , bubbled air, I_2 , NaClO_2 , NaClO_3 , KClO_3 , NH_4ClO_3 , NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , $\text{Ca}(\text{ClO})_2$, Cl_2 , CuCl_2 , FeCl_3 , CaO_2 , sodium iodate, potassium iodate, manganese dioxide, perchloric acid, or combinations thereof. The oxidant may comprise KClO_3 , NH_4ClO_3 , NaClO_3 .

[0083] The concentration and/or amount of second oxidant used may be selected at least in part based on the type of platinum group metal contaminants to be precipitated, the amount of platinum group metal contaminants to be precipitated, and/or the oxidant being used. The oxidant may be in solution, for example an aqueous solution, and the concentration of the oxidant in solution is at least 10%, or at least 20%, or at least 30%. The oxidant may be used neat, and may be contacted with the contaminants at a stoichiometric amount, or a greater than stoichiometric amount.

[0084] The polyatomic salt may be any polyatomic salt suitable for counter-ion exchanging with complexes of platinum group metals, such as complexes of palladium or platinum. The polyatomic salt may comprise an ammonium salt. The ammonium salt may comprise ammonium chloride, ammonium sulfate, ammonium nitrate, or combinations thereof. The ammonium salt may comprise ammonium chloride, ammonium nitrate, or combinations thereof. The ammonium salt may comprise ammonium chloride.

[0085] The concentration and/or amount of polyatomic salt used may be selected at least in part based on the type of platinum group metal contaminants to be precipitated, the amount of platinum group metal contaminants to be precipitated, and/or the polyatomic salt being used. The polyatomic salt may be in solution, for example an aqueous solution, and the concentration of the polyatomic salt in solution may be at least 0.1 M, or at least 1M, or at least 5M, or at least 10M. The polyatomic salt may be used neat, and is added to the leached solution in an amount stoichiometric to the platinum group metal contaminants, or a greater than stoichiometric amount.

[0086] Depending on (i) the original purity of the precious metal; (ii) the desired purity of the refined precious metal; (iii) the material from which the precious metal is sourced; and/or (iv)

what is other metals, salts, compounds, components, etc. may be present in said material, including the precipitation step in the refining method described herein may facilitate reaching precious metal purity levels of $\geq 99.9\%$, or $\geq 99.99\%$. Depending on (i) the original purity of the precious metal; (ii) the desired purity of the refined precious metal; (iii) the material from which the precious metal is sourced; and/or (iv) what is other metals, salts, compounds, components, etc. may be present in said material, excluding the precipitation step in the refining method described herein may not impact whether precious metal purity levels of $\geq 99.9\%$, or $\geq 99.99\%$ may be reached.

10 [0087] Filtration and Rinse Steps

[0088] The refining method as described herein further comprises filtering the leached solution prior to reducing the leached precious metal. As the precious metal is being leached into the refining solution, some of the material from which the precious was sourced may remain undissolved; impurities or contaminants within the precious metal itself (for example, 15 metals such as Ag, Pb, Sn, Zn, Al, Pd, Pt, Fe, Cu, Co, Ni, Al, etc.) may remain undissolved; and/or solids, such as salt by-products of the leaching reaction, may precipitate out of the refining solution. When such undissolved solids remain, or such precipitated solids occur, separating the leached solution from said solids may assist in achieving precious metal purities of 999, 999+, 9999, or 9999+.

20 [0089] The refining method as described herein further comprises rinsing the reduced precious metal, once separated from the leached solution. The refining method as described herein may further comprise rinsing the precious metal prior to being added to the refining solution. Such rinses may wash away remaining leached solution and/or other solutions or chemicals associated with leaching and/or reducing the precious metal. Such rinses may 25 remove surface contaminants from the precious metal or reduced precious metal, which may further increase purity. Such rinses may leach contaminants from the precious metal or reduced precious metal, which may further increase purity. Such rinses may wash away, leach, and/or solubilize contaminants from the surface of the precious metal or reduced precious metal, which may further increase purity.

30 [0090] Rinsing the precious metal or reduced precious metal may comprise washing the metal with water, an aqueous solution, or a combination thereof. Rinsing the precious metal or reduced precious metal may comprise washing the metal with the solvent of the refining solution. Rinsing the precious metal or reduced precious metal with the solvent of the refining

solution may comprise rinsing with glacial acetic acid, acetic acid, aqueous solutions thereof, and/or combinations thereof. Rinsing the precious metal or reduced precious metal may comprise rinsing the metal with a rinse solution. The rinse solution may comprises a rinse acid, a rinse complexing agent, or a combination thereof. The rinse solution may comprise a rinse acid and a rinse complexing agent. The rinse complexing agent may comprise the reductant as described herein and above. Rinsing the precious metal or reduced precious metal may comprise rinsing with water, an aqueous solution, or a combination thereof; the solvent of the refining solution; the rinse solution; or a combination thereof. Rinsing the precious metal or reduced precious metal may comprise dosing the precious metal with water, an aqueous solution, or a combination thereof; then dosing the precious metal with the rinse acid; and then dosing the precious metal with the rinse complexing agent - thereby forming the rinse solution - the then flowing the so-formed rinse solution through the reduced, precipitated precious metal to rinse it. Rinsing the precious metal or reduced precious metal may comprise dosing the precious metal with water, an aqueous solution, or a combination thereof; then dosing the precious metal with the rinse acid; and then dosing the precious metal with the rinse complexing agent wherein the rinse complexing agent comprises the reductant described herein - thereby forming the rinse solution - the then flowing the so-formed rinse solution through the reduced, precipitated precious metal to rinse the precious metal.

[0091] The contaminants may comprise transition metal salts or transition metal complexes. The contaminants may comprise transition metal salts or transition metal complexes that are not inclusive of the desired precious metal. The rinse complexing agent may be suitable for ligand exchange with said transition metal salts or transition metal complexes, such that a new transition metal salt or complex is formed with the rinse complexing agent acting as ligand. The complexation reagent may be selective of said transition metals over the precious metals, such that complexation of the precious metals by the complexation reagent is reduced or prevented. With the rinse complexing agent acting as ligand, said transition metal salts or complexes may become soluble in aqueous solution or acidic aqueous solution, thereby permitting their leaching or separation from the precious metal.

[0092] The rinse complexing agent of the rinse solution may thus be any complexing agent suitable for complexing the contaminants being removed. A suitable complexing agent may be selected in view of (i) the desired purity of the refined precious metal; and/or (ii) what other

contaminants, metals, salts, compounds, components, etc. may be present in the precious metal or reduced precious metal .

[0093] For example, where a 999+ or 9999+ purity is desired for a refined precious metal, a rinse complexing agent may be selected that will not introduce its own contaminants into the refining method (by-products of its synthesis, its counter ion(s), etc.). Where one complexing agent may not suitably complex transition metal contaminants that are in the precious metal, or may remain in the reduced precious metal, another more suited for complexation may be selected.

[0094] The rinse complexing agent may comprise a thiourea, a thiosulfate, or a combination thereof. The rinse complexing agent may have a concentration of about 0.1 M to about 4 M, or about 0.1 M to about 3 M, or about 0.1 M to about 2 M, or about 0.1 M to about 1 M, or about 0.1 M to about 0.5 M, or about 0.1 to about 0.4 M, or about 0.1 M to about 0.3 M, or about 0.1 to about 0.2 M; or is at any concentration or any range of concentrations within about 0.1 M and about 4 M. The contaminants may comprise transition metals. The transition metals comprise late transition metals. The transition metals may comprise Ag, Pb, Sn, Zn, Al, Pd, Pt, Fe, Cu, Co, Ni, Al, or a combination thereof. The contaminant may be Ag; and once complexed with the complexation reagent, the Ag contaminant becomes water soluble and thus more readily removable.

[0095] The rinse acid of the rinse solution may be any proton donor suitable for the contaminants being removed. A suitable rinse acid may be selected in view of (i) the desired purity of the refined precious metal; and/or (ii) what other metals, salts, compounds, components, etc. may be present in the reduced precious metal .

[0096] For example, where a 999+ or 9999+ purity is desired for a refined precious metal, a rinse acid may be selected that will not introduce its own contaminants into the refining method (by-products of its synthesis, its counter ion(s), etc.). Where one rinse acid may react with (i) components or chemicals used during the refining method; and/or (ii) other metals, salts, compounds, components, etc. that may remain in the reduced precious metal to form noxious or toxic by-products (for example, NO_x gas being formed from HNO_3), then another rinse acid may be selected that will not form such by-products.

[0097] The rinse acid may be a suitably strong acid. The rinse acid may have a pK_a of <3 , or <2.5 , or <2 , or <1 , or <0 . The rinse acid may comprise HCl, HBr, HI, chlorous acid, chloric acid, bromous acid, bromic acid, iodous acid, iodic acid, perchloric acid, sulfuric acid, nitric acid, oxalic acid, phosphoric acid, methanesulfonic acid, citric acid, an organic acid, or combinations thereof. The acid may comprise HCl, sulfuric acid, nitric acid, or a combination

thereof. The rinse acid may comprise HCl. The rinse acid may have a concentration of about 0.01 M to about 10 M; or has any concentration or any range of concentrations within about 0.01 M and about 10 M. The rinse acid may have a concentration of about 0.01 M to about 10 M; or about 0.01 M to about 8 M; or about 0.01 M to about 6 M; or about 0.01 M to about 4 M.

5 [0098] As noted above, the rinse solution may be selected based on the contaminants to be removed. A rinse solution comprising HNO_3 as a rinse acid may be selected if the precious metal or reduced precious metal have higher concentrations of Pb, Cu, Fe, and/or Ni contaminants - as HNO_3 may remove these contaminants with little to no dissolution of the precious metal. However, a rinse solution comprising HNO_3 may not be selected if there are
10 concerns HNO_3 could react with components or chemicals used during the refining method to form NO_x .

[0099] A rinse solution comprising HCl as a rinse acid may be selected if the precious metal or reduced precious metal have higher concentrations of Fe, Pb, Cu, and/or Fe contaminants - as HCl may remove these contaminants with little to no dissolution of the
15 precious metal.

[00100] A rinse solution comprising *sodium thiosulfate* as a rinse complexing agent may be selected if the precious metal or reduced precious metal have higher concentrations of Pd contaminants - as *sodium thiosulfate* may remove this contaminant with little to no dissolution of the precious metal. However, a rinse solution comprising *sodium thiosulfate* may not be
20 selected if there are concerns *sodium thiosulfate* could react with components or chemicals used during the refining method to decomposes into SO_2 gas and elemental sulfur.

[00101] A rinse solution comprising *thiourea* as a rinse complexing agent may be selected if the precious metal or reduced precious metal have higher concentrations of Ag contaminants - as *thiourea* may remove this contaminant with little to no dissolution of the
25 precious metal.

[00102] A rinse solution comprising a combination of rinse acid and rinse complexing agent may be selected to combine the components' respective rinsing properties. A rinse solution comprising HCl and *thiourea* may be selected to leverage HCl 's ability to remove of Fe, Pb, Cu, and/or Fe with thiourea's ability to remove Ag.

30

[00103] **Conditions of the Refining Methods**

[00104] Conditions under which the herein described refining methods are run may vary depending on the step, or stage of the refining method.

[00105] During the stage where the precious metal is being added to the refining solution, the phase ratio of refining solution to precious metal may be about 3 to about 1, or about 4 to about 1, or about 5 to about 1, or about 6 to about 1, or about 7 to about 1, or about 8 to about 1, or about 9 to about 1, or about 10 to about 1. The phase ratio of refining solution to precious metal may be about 5.2 to about 1; 5.3 to about 1; 5.4 to about 1; or about 5.5 to about 1; about 5.6 to about 1; 5.7 to about 1; 5.8 to about 1; 5.9 to about 1; or about 6 to about 1. The phase ratio of refining solution to precious metal may be about 3-10 (solution) to 1 (metal); or may be any phase ratio between about 3-10 (solvent) to 1 (metal).

[00106] During the stage where the precious metal is being leached into the refining solution, the leaching reaction may occur at a leaching temperature or within a leaching temperature range. Said leaching temperature or temperature range may be greater than ambient temperature to improve, or increase rate at which the leaching occurs. Said leaching temperature or temperature range may be less than the boiling point of the refining solution at ambient pressures, to reduce or avoid solution loss. The leaching reaction may be exothermic. As such, the temperature at which the leaching occurs may be controlled by managing the rate at which the precious metal and/or components of the refining solution are added or combined. Under circumstances where the leaching reaction may not be sufficiently exothermic to maintain the leaching temperature or temperature range, the temperature at which the leaching stage occurs may be controlled by heating the refining solution using external heating sources, such as heating mantles, heating blankets, etc. The leaching temperature or temperature range at which the leaching occurs may be about 20 °C to about 80 °C, about 20°C to about 60°C, about 20°C to about 40°C, or about 20°C to about 25°C; or may be at any temperature, or any range of temperatures between about 20°C and about 80°C.

[00107] During the stage where the precious metal is being reduced from the leached solution, the reducing reaction may occur at a reducing temperature or within a leaching temperature range. Said reducing temperature or temperature range may be greater than ambient temperature to improve, or increase rate at which the reduction occurs. Said reducing temperature or temperature range may be less than the boiling point of the leached solution at ambient pressures, to reduce or avoid solution loss. The temperature at which the reducing stage occurs may be controlled by heating the leached solution using external heating sources, such as heating mantles, heating blankets, etc. The reducing temperature or temperature range at which reduction occurs may be about 35°C to about 75°C; or about 40°C to about 70°C; or about 45°C to about 65°C; or about 50°C to about 65°C; or about 55°C to about 65°C;

or about 60°C; or may be at any temperature, or any range of temperatures between about 35°C and about 75°C.

[00108] During the stage where the precious metal is being reduced from the leached solution, the reducing reaction may further comprise a catalyst to improve, or increase rate at which the reduction occurs. The catalyst may comprise a base catalyst. A suitable base catalyst may be selected in view of (i) the desired purity of the refined precious metal (for example, to reduce or avoid introducing additional, unwanted components/contaminants into the leached solution); and/or (ii) what other metals, salts, compounds, components, etc. may be present in the precious metal and/or leached solution (for example, to reduce or avoid formation of unwanted or unsafe by-products). The base catalyst may comprise an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkali metal bicarbonate, an alkaline earth metal bicarbonate, an alkali metal carbonate, an alkaline earth metal carbonate, or a combination thereof. The base catalyst may comprise sodium hydroxide, sodium bicarbonate, sodium carbonate, or a combination thereof. The base catalyst may be dosed into the leached solution during reduction. The base catalyst may be dosed into the leached solution a period of time after reduction begins. That period of time may be about 1 min to about 20 min, or for a period of time of about 10 min. The base catalyst may be dosed continuously, or at discrete time intervals. If the base catalyst is continuously dosed, the base catalyst may be continuously dosed into the leached solution for the remainder of the reduction reaction. The base catalyst may be continuously dosed into the leached solution for a period of about 1 min to about 10 min. The period of time may be selected based on the amount of precious metal to be reduced, and may be modified is insufficient amounts of precious metal precipitate, or if the reduction is taking too long. If the base catalyst is dosed discreetly at specific time intervals - after an initial dose of base catalyst is added to the leached solution - additional base catalyst may be added at 1 min intervals, 3 min intervals, 5 min intervals, 8 min intervals, 10 min intervals, etc. After the initial dose, the base catalyst may be dosed into the refining solution 1 more time, 2 more times, 3 more time, 4 more times, etc. The number of base catalyst doses and length of each time interval may be selected based on: the amount of precious metal to be dissolved; the desired rate of reducing the precious metal, etc.; controlling pH increase to reduce or prevent additional contaminants being precipitated out; and may be modified should insufficient amounts of precious metal precipitate.

[00109] During the stage where the precious metal or reduced precious metal are being rinsed, the water, aqueous solution, or a combination thereof and/or rinsing solution may be at

a rinsing temperature greater than ambient temperature and less than the boiling point of the rinse. Rinsing with a solution at a rinsing temperature greater than ambient temperature may increase solubility of contaminants *into* the rinse, which may facilitate reaching the desired purity for the refined precious metal. Rinsing with a solution at a rinsing temperature greater than ambient temperature may increase the rate at which contaminants are leached *into* the rinse, which may also facilitate reaching the desired purity for the refined precious metal.

[00110] At any stage of the refining method described herein, there may be stirring and/or agitation to facilitate dispersion, homogenization, mass transfer, reaction kinetics, etc.

[00111] The amount of time that leaching is conducted may be until a sufficient amount, most, or all precious metal is dissolved or leached. This may be tested spectrometrically, or visually. Conditions such as temperature and stirring/agitation may be controlled to manage timing. The amount of time that reduction is conducted may be until a sufficient amount, most, or all precious metal is precipitated. This may be tested spectrometrically, or visually. Conditions such as temperature and stirring/agitation may be controlled to manage timing.

[00112] **Feedstock**

[00113] The material from which the precious metal is sourced is also referred to herein as a feedstock. The refining method described herein may be used to process feedstocks comprising metal concentrate, metal ore, electronic waste, jewelry, Doré bars, metal shavings, metal scraps, hydrometallurgically-produced metals and/or metal waste, pyrometallurgical-produced metals and/or metal waste, any metal-containing product, device, and/or implement, or a combination thereof. The jewelry may comprise a precious metal that is 8 karat, 10 karat, 14 karat, or a combination thereof.

[00114] The feedstock may comprise a precious metal having starting purity of <90%, and the herein described refining method is applied to improve said purity to ≥99%, ≥99.9%, about 99.99%, or ≥99.99%. The feedstock may comprise a precious metal having starting purity of ≥99%, ≥99.9%, and the herein described refining method is applied to improve said purity to about 99.99%, or ≥99.99%.

[00115] The feedstock may comprise gold (Au), platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir), osmium (Os), or a combination thereof. The feedstock may comprise gold (Au), platinum (Pt), palladium (Pd), or a combination thereof. The precious metal to be leached and/or collected from the feedstock via methods described herein may comprise gold (Au), platinum (Pt), palladium (Pd), or a combination thereof. The precious metal to be

leached and/or collected from the feedstock via methods described herein may comprise gold (Au). The precious metal to be leached from the feedstock and refined via methods described herein may comprise gold (Au). The precious metal to be leached from the feedstock and refined via methods described herein to a purity of about $\geq 99\%$, about $\geq 99.9\%$, or about $\geq 99.99\%$. may comprise gold (Au).

[00116] Refining Method as Described herein

[00117] At least in view of the forgoing, there is provided herein method of refining a precious metal, the method comprising forming a refining solution, where the refining solution comprises an acid in a partially water-miscible or water-miscible solvent; adding a precious metal to the refining solution; dosing an oxidant into the refining solution; leaching the precious metal into the refining solution; and forming a leached solution comprising leached precious metal.

[00118] Dosing an oxidant into the refining solution may comprise continuously dosing the oxidant into the refining solution over a period of time; and/or dosing the oxidant at time intervals. Continuously dosing the oxidant into the refining solution over a period of time may comprises dosing the oxidant into the refining solution for the duration of leaching the precious metal into the refining solution; or dosing the oxidant into the refining solution for a period of time that is less than the duration of leaching the precious metal into the refining solution. Dosing the oxidant at time intervals may comprises adding a first dose of the oxidant to the refining solution when forming the refining mixture; and adding subsequent doses of the oxidant to the refining solution at intervals of time after adding the first dose. Adding subsequent doses of the oxidant may comprise adding two or more additional doses of oxidant. Each of the intervals of time after adding the first dose may be about 1 min to about 5 min; or about 1 min to about 4 min; or about 1 min to about 3 min; or about 1 min to 2 min; or about 1 min.

[00119] The method may further comprise filtering the leached solution to remove undissolved solids, precipitated solids, or a combination thereof.

[00120] The method may further comprise adding a reductant to the leached solution; and reducing the leached precious metal; and precipitating reduced precious metal. Adding a reductant to the leached solution may further comprise adding a first dose of a base to the leached solution a first period of time after adding the reductant; and optionally adding a second dose of the base a second period of time after adding the first dose of base. The first

period of time and/or the second period of time may be about 1 to about 10 min; or about 3 to about 10 min; or about 7 to about 10 min. The reductant may comprise thiourea, sodium metabisulfite, sodium sulfite, or a combination. The reductant may comprise aqueous solutions of thiourea, sodium metabisulfite, sodium sulfite, or a combination. The reductant may
5 comprise an aqueous solution of thiourea.

[00121] Adding a reductant to the leached solution and reducing the leached precious metal may comprises heating the leached solution. Heating the leached solution may comprise bring the leached solution to a temperature above ambient temperature and below the boiling point of the leached solution. Heating the leached solution may comprise bringing the leached
10 solution to a temperature of about 35°C to about 75°C; or about 40°C to about 70°C; or about 45°C to about 65°C; or about 50°C to about 65°C; or about 55°C to about 65°C; or about 60°C.

[00122] The method may further comprise separating the reduced precious metal from the leached solution.

[00123] The method may further comprise washing the reduced precious metal with
15 water, an aqueous solution, or a combination thereof.

[00124] The method may further comprise rinsing the reduced precious metal with a rinse solution to form a refined precious metal. The rinse solution may comprise a rinse acid, a rinse complexing agent, or a combination thereof. The rinse solution may comprise a rinse acid and a rinse complexing agent. The rinse acid may comprise hydrochloric acid, nitric acid,
20 sulfuric acid, or a combination thereof. The rinse complexing agent may comprise a thiourea, a thiosulfate, or a combination. The rinse solution may comprise an aqueous solution of thiourea and hydrochloric acid.

[00125] Rinsing the reduced precious metal with a rinse solution may comprise heating the rinse solution. Heating the rinse solution comprises bringing the rinse solution to a
25 temperature above ambient temperature and below the boiling point of the rinse solution. Heating the rinse solution may comprise bring the rinse solution to a temperature of about 35°C to about 75°C; or about 40°C to about 70°C; or about 45°C to about 65°C; or about 50°C to about 65°C; or about 50°C to about 60°C; or about 60°C.

[00126] The method may further comprise washing the refined precious metal with
30 water, an aqueous solution, or a combination thereof.

[00127] The method may comprise forming the refining solution, adding the precious metal to the refining solution, and dosing the oxidant into the refining solution by combining the acid, a first dose of the oxidant, and a ligand source in the partially water-miscible or water-

miscible solvent; and then adding the precious metal. The ligand source may comprise a chloride salt. The ligand source may comprise MgCl_2 , AlCl_3 , CaCl_2 , or a combination thereof.

[00128] The method may further comprise recharging the refining solution with a final dose of the oxidant and a second dose of the acid.

- 5 **[00129]** The method may further comprise adding a second oxidant and a polyatomic salt to the leached solution to precipitate contaminants from the leached solution. The polyatomic salt may comprises an ammonium salt. The polyatomic salt may comprise ammonium chloride, ammonium sulfate, ammonium nitrate, or combinations thereof. The second oxidant may comprise HNO_3 , H_2O_2 , O_2 , bubbled air, I_2 , NaClO_2 , NaClO_3 , KClO_3 ,
10 NH_4ClO_3 , NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , $\text{Ca}(\text{ClO})_2$, Cl_2 , CuCl_2 , FeCl_3 , CaO_2 , sodium iodate, potassium iodate, manganese dioxide, perchloric acid, or combinations thereof. The second oxidant may comprise KClO_3 , NH_4ClO_3 , NaClO_3 . The second oxidant may comprise NaClO_3 .

- [00130]** The acid of the refining solution may comprise HCl , HBr , HI , chlorous acid, chloric acid, bromous acid, bromic acid, iodous acid, iodic acid, perchloric acid, sulfuric acid,
15 nitric acid, oxalic acid, phosphoric acid, an organic acid, or combinations thereof. The acid of the refining solution may comprise HCl , HBr , HI . The acid of the refining solution may comprise HCl .

- [00131]** The oxidant of the refining solution may comprise HNO_3 , H_2O_2 , O_2 , bubbled air, I_2 , NaClO_2 , NaClO_3 , KClO_3 , NH_4ClO_3 , NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , $\text{Ca}(\text{ClO})_2$, Cl_2 , CuCl_2 , FeCl_3 ,
20 CaO_2 , sodium iodate, potassium iodate, manganese dioxide, perchloric acid, or combinations thereof. The oxidant may comprise KClO_3 , NH_4ClO_3 , NaClO_3 . The oxidant comprises NaClO_3 .

- [00132]** The partially water-miscible or water-miscible solvent may comprise glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, or a combination thereof. The partially water-miscible or water-miscible solvent may comprise aqueous solutions of glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, or a combination thereof. The partially water-miscible or water-miscible solvent may comprises glacial acetic acid; acetic acid; an aqueous solution of glacial acetic acid; and aqueous solution of acetic acid; or a combination thereof. The partially water-miscible or water-miscible solvent may comprise glacial acetic acid; an aqueous solution of glacial acetic acid; or a combination thereof. The aqueous solution of
25 glacial acetic acid may comprise about 20% by volume to about 30% by volume glacial acetic acid.
30

- [00133] The precious metal to which the method is applied may comprise Au, Pt, Pd, Rh, Ru, Ir, Os, or a combination thereof. The precious metal may comprise Au, Pd, Pt, Rh, or a combination thereof. The precious metal may comprise Au.
- [00134] The final purity of the refined precious metal formed from the method may be a
- 5 purity of $\geq 99\%$, $\geq 99.9\%$, or $\geq 99.99\%$.

- [00135] In one or more embodiments, the herein described refining method may be conducted as follows:
- [00136] The precious metal to be refined comprises gold. The gold is rinsed and then
- 10 subject to leaching according to the following recipe:

Refining Leach Recipe (m_{Au} = Mass of gold in grams)	
Phase Ratio (L:S)	5.5
<i>Solvent</i>	$3m_{Au}$ in mL
<i>Acid</i>	$2m_{Au}$ in mL (4.4 mol/L)
<i>Oxidant</i> _{initial}	$(0.5m_{Au})/3$ in mL
<i>Oxidant</i> _{dose} • Dose Oxidant at 1 & 2 minutes	$(0.5m_{Au})/3$ in mL

- [00137] For lab-scale work, agitation with a stir bar on a stir plate set to approx. 700 rpm was found to be sufficient for complete leaching of gold powder.
- [00138] After the final dose of *oxidant* at 2 minutes, the reaction is allowed to continue
- 15 for a total time of 10 minutes or until no solid gold powder is visible, whichever is longer.
- [00139] Once leaching is complete, use a Büchner funnel and two layers of filter paper to vacuum-filter the solution. The beaker and filter cake may be rinsed with a small amount (no more than 10% of the filtrate volume) of *solvent* to reduce the amount of gold loss.
- [00140] Reserve the filtrate in a clean beaker and discard the collected solid.
- 20 [00141] Gold Reduction
- [00142] Prepare a 60°C hot water bath in an appropriately sized beaker, with enough water to completely submerge the expected liquid level in the reaction vessel. The temperature of the bath shall be confirmed via thermocouple.
- [00143] Place the reduction vessel into the hot water bath. Using a clean stir bar, agitate
- 25 the filtrate from 5.3.1 at around 700 rpm, while the solution acclimatizes to the hot water bath.

- [00144] Gold will be precipitated from solution, leaving most of the remaining impurities in solution, using a *reductant such as thiourea*; the amount of *thiourea* required is about 0.2 times the amount of gold in solution in grams. *For example, if 5 g of gold was leached, 1 g of thiourea is required.*
- 5 [00145] Weigh the required amount of *thiourea* and dissolve in 7.04 mL H₂O per gram of *thiourea*. It is possible that a small amount of *thiourea* may not dissolve. This may be remedied by heating the solution on a hot plate set to 75°C while stirring. Alternatively, a stock solution of saturated *thiourea* solution may be prepared and used as necessary.
- [00146] Once the leach solution has reached 60°C, verified via thermocouple, increase
10 agitation to 1000 rpm and add the required amount of *thiourea* solution to the beaker containing the leach solution.
- [00147] After 60 minutes of stirring, check the progress of the precipitation by analyzing the solution on ICP-OES at 100x and 1000x dilution in 5% ultra-pure nitric acid. For a relatively more accurate measurement, aliquot 5-10 mL of solution into a 40 mL vial and centrifuge for 2
15 minutes at 1700 rpm before preparing ICP samples. Return any excess sample to the precipitation vessel to reduce, prevent, or minimize gold loss. The Au in solution should read <1000 mg/L. If it is >1000 mg/L, the solution may be left to agitate for additional time, checking the Au in solution periodically.
- [00148] Once the precipitation is complete, use a Büchner funnel and two layers of P4
20 filter paper to filter the solution. Replace the filtration flask with a clean filtration flask and wash the gold cake with approximately 5-20 x the mass of expected gold of *water*. Some of this *water* may be used to rinse the precipitation vessel onto the gold cake to reduce, prevent, or minimize gold loss. If any non-gold solid remains, wash the cake sparingly with *water* using a wash bottle.
- 25 [00149] Replace the filtration flask with a clean filtration flask, leaving the gold cake in place in the Büchner funnel. *Water* rinses may be discarded in aqueous waste.
- [00150] Thiourea Rinse
- [00151] Prepare sufficient 1.0 mol/L *thiourea* solution to wash the collected gold with a 5:1 phase ratio by dissolving *thiourea* in 13.1 mL of 0.5 mol/L *acid (HCl)* per gram of *thiourea*.
30 For example, if there is 5 g of gold to be washed, prepare 25 mL of 1.0 mol/L *thiourea* solution by dissolving 1.9 g of *thiourea* in 25 mL of 0.5 mol/L *acid* solution.
- [00152] Wash the gold by pouring the entirety of the *thiourea/acid* solution overtop the gold cake in the filtration apparatus.

[00153] Analyze the filtrate using ICP-OES (10x dilution in 5% ultra-pure nitric acid) to determine the amount of silver in solution.

[00154] Once washing with *thiourea/acid* is completed, replace the filtration flask and rinse the gold twice with *water* in a 5:1 phase ratio.

5 [00155] Collect and dry the refined gold. *Thiourea* and *water* rinses may be disposed in aqueous waste.

[00156] Gold Purity

[00157] Determine the purity of the refined gold by digesting 0.1 g of gold solid in 20 mL of reverse aqua regia (1:3 ultra-pure HCl:HNO₃ by volume) and analyzing on ICP-OES at 2x,
10 10x, and 1,000x dilutions using 5% ultra-pure nitric acid.

[00158] Purity may be determined using Formula 1:

$$Purity \% = \left(\frac{1,000,000 - SUM \left(Impurities \text{ in } \frac{mg}{kg} \right)}{1,000,000} \right) * 100\% \quad (1)$$

[0001] *Use the lowest dilution possible, usually 2x, for the determination of the impurities*

15

[00159] **Refining Methods**

[00160] In one or more embodiments of the refining method described herein, there is provided a method of refining a precious metal. In one or more embodiments, the method comprises contacting the precious metal with a refining solution under conditions to solubilize
20 the precious metal, and forming a leach solution comprising leached precious metal. In one or more embodiments, the refining solution comprises an acid, an oxidant, a ligand source, and a partially water-miscible or water-miscible organic solvent.

[00161] Precious metals subjected to the herein described refining method may be extracted from any substance comprising precious metal, using any method suitable for doing
25 so. The substance comprising precious may comprise metal concentrate, metal ore, electronic waste, jewelry, metal shavings, metal scraps, hydrometallurgically-produced metals and/or metal waste, pyrometallurgical-produced metals and/or metal waste, any metal-containing product, device, and/or implement, or a combination thereof.

[00162] The method as described herein may further comprise contacting the leach solution with a reductant, and precipitating the leached precious metal. The reductant may comprise sodium metabisulfite, Fe(II)Cl_2 , ascorbic acid, oxalic acid, hydrazine, hydrazine hydrochloride, hydroxylamine, hydroxylamine hydrochloride, or a combination thereof.

- 5 [00163] The method as described herein may further comprise contacting the precipitated precious metal with a rinse solution for dissolving contaminants and forming a refined precious metal, the rinse solution comprising a complexation reagent.

- [00164] Contaminants may comprise transition metal salts or transition metal complexes. Contaminants may comprise transition metal salts or transition metal complexes that are not inclusive of the desired precious metals. The complexation reagent may be suitable for ligand exchange with said transition metal salts or transition metal complexes, such that a new transition metal salt or complex is formed with the complexation reagent acting as ligand. The complexation reagent may be selective of said transition metals over the previous metals, such that complexation of the precious metals by the complexation reagent is reduced, prevented, or minimized. With the complexation reagent acting as ligand, said transition metal salts or complexes may become soluble in aqueous solution or acidic aqueous solution, thereby permitting their separation from the precious metal.
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- [00165] The complexation reagent may comprise a thiourea, a thiosulfate, or a combination. The rinse solution comprising a complexation reagent may comprise a solution of thiourea and one or more of hydrochloric acid, nitric acid, sulfuric acid. The rinse solution comprising a complexation reagent may comprise a solution of sodium thiosulfate and one or more of sodium bicarbonate, sodium carbonate, Ca(OH)_2 . The contaminants may comprise transition metals. The transition metals comprise late transition metals. The transition metals may comprise Ag, Pb, Sn, Zn, Al, Pd, Pt, Fe, Cu, Co, Ni, Al, or a combination thereof. In one or more embodiments, the contaminant may be Ag; and once complexed with the complexation reagent, the Ag contaminant becomes water soluble and thus more readily removable.
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[00166] The method as described herein may further comprise washing the refined precious metal with an aqueous solution.

- [00167] The method as described herein may further comprise pre-rinsing the precious metal prior to contacting with the refining solution. The pre-rinsing may comprise contacting the precious metal with a dilute acidic solution; contacting the acid-washed precious metal with an aqueous solution; and contacting the aqueous-washed precious metal with a concentrated
- 30

acid. The dilute acidic solution may comprise HCl, HBr, HI, HNO₃, H₂SO₄, H₃PO₄, or a combination thereof. The concentrated acid may comprise glacial acetic acid.

[00168] Pre-rinsing the precious metal may initially clean the precious metal prior to being contacted with the refining solution. Pre-rinsing may remove one or more contaminants from the precious metal before being contacted with the refining solution. The one or more contaminants may include base metals or ferrous metals. The base or ferrous metals may include Pb, Fe, Sn, Zn, Cu, Al, Ni, or a combination thereof.

[00169] When contacting the precious metal with the refining solution, the method as described herein may further comprises dosing the refining solution with additional oxidant. Contacting the precious metal with the refining solution may further comprises dosing the refining solution with additional oxidant at least once, or at least twice after contacting the precious metal with the refining solution.

[00170] The refining solution as used herein may have a phase ratio up to about 3:1, or up to about 5:1, or up to about 7:1, or up to about 10:1, wherein the ratio of refining solution to precious metal is up to about 3 to about 1, or about 5 to about 1, or about 7 to about 1, or about 10 to about 1. The refining solution as used herein may have a 5.5:1 phase ratio, wherein the ratio of refining solution to precious metal is about 5.5 to about 1.

[00171] The acid of the refining solution may comprise HCl, HBr, HI, chlorous acid, chloric acid, bromous acid, bromic acid, iodous acid, iodic acid, perchloric acid, sulfuric acid, nitric acid, oxalic acid, phosphoric acid, an organic acid, or combinations thereof. The acid of the refining solution may comprise HCl, HBr, HI. The acid of the refining solution may comprise HCl.

[00172] The oxidant of the refining solution may comprise HNO₃, H₂O₂, O₂, bubbled air, I₂, NaClO₂, NaClO₃, KClO₃, NH₄ClO₃, NaClO, K₂Cr₂O₇, KMnO₄, Ca(ClO)₂, Cl₂, CuCl₂, FeCl₃, CaO₂, sodium iodate, potassium iodate, manganese dioxide, perchloric acid, or combinations thereof. The oxidant of the refining solution may comprise KClO₃, NH₄ClO₃, NaClO₃. The oxidant of the refining solution may comprise NaClO₃.

[00173] The ligand source of the refining solution may comprise a chloride salt. The ligand source of the refining solution may comprise HCl, MgCl₂, AlCl₃, CaCl₂, or a combination thereof. The ligand source of the refining solution may comprise MgCl₂.

[00174] The partially water-miscible or water-miscible organic solvent of the refining solution may comprise glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, or a combination thereof. The partially water-miscible or water-miscible organic solvent of the

refining solution may comprise glacial acetic acid, acetic acid, or a combination thereof. The partially water-miscible or water-miscible organic solvent of the refining solution may comprise glacial acetic acid.

5 [00175] The precious metal of the method described herein may comprise Au, Pt, Pd, Rh, Ru, Ir, Os, or a combination thereof. The precious metal may comprise Au, Pd, Pt, Rh, or a combination thereof. The precious metal may comprise Au.

[00176] The refined precious metal of the method described herein may comprise a purity of $\geq 99\%$, or $\geq 99.9\%$.

10 [00177] In one or more embodiments described herein, there is also provided:

1. A method of refining a precious metal, the method comprising
preparing a refining solution, the preparation comprising adding an acid and a ligand source to a partially water-miscible or water-miscible solvent to form a first solution, and adding an oxidant to the first solution to form the refining solution;
- 15 contacting a precious metal with the refining solution, the contacting comprising adding a first additional dose of the oxidant to the refining solution in contact with the precious metal after a first period of time, and adding a second additional dose of the oxidant to the refining solution in contact with the precious metal after a second period of time; and forming a leached solution comprising a leached precious metal.
- 20 2. The method of claim 1, wherein the first period of time starts at the contacting of the precious metal with the refining solution.
3. The method of any preceding embodiment, wherein the second period of time starts at the adding of the first additional dose of the oxidant to the refining solution.
4. The method of any preceding embodiment, wherein the first period of time is about 1
25 to about 5 min; or about 1 to about 4 min; or about 1 to about 3 min.
5. The method of any preceding embodiment, wherein the second period of time is about 1 to about 5 min; or about 1 to about 4 min; or about 1 to about 3 min.
6. The method of any preceding embodiment, wherein adding the oxidant, adding the first additional dose of the oxidant, and the second additional dose of the oxidant comprises
30 continuously dosing the oxidant into the refining solution over a period of time.
7. The method of any preceding embodiment, wherein continuously dosing the oxidant into the refining solution over a period of time comprises dosing the oxidant into the refining solution for the duration of leaching the precious metal into the refining solution; or dosing the

oxidant into the refining solution for a period of time that is less than the duration of leaching the precious metal into the refining solution.

8. The method of any preceding embodiment, further comprising contacting the leached solution with a reductant, and precipitating the leached precious metal to form precipitated precious metal.
9. The method of the preceding embodiment, wherein the reductant comprises sodium metabisulfite, Fe(II)Cl_2 , ascorbic acid, oxalic acid, hydrazine, hydrazine hydrochloride, hydroxylamine, hydroxylamine hydrochloride, or a combination thereof.
10. The method of any preceding embodiment, further comprising washing the precipitated precious metal with water, an aqueous solution, or a combination thereof.
11. The method of any preceding embodiment, further comprising contacting the precipitated precious metal with a rinse solution for dissolving contaminants, the rinse solution comprising a complexation reagent; and forming a refined precious metal.
12. The method of the preceding embodiment, wherein the complexation reagent comprises a thiourea, a thiosulfate, or a combination.
13. The method of any preceding embodiment, wherein the rinse solution comprising a complexation reagent comprises a solution of thiourea and one or more of hydrochloric acid, nitric acid, sulfuric acid.
14. The method of any preceding embodiment, wherein the rinse solution comprising a complexation reagent comprises a solution of sodium thiosulfate and one or more of sodium bicarbonate, sodium carbonate, Ca(OH)_2 .
15. The method of any preceding embodiment, wherein the contaminants comprise transition metals.
16. The method of the preceding embodiment, wherein the transition metals comprise late transition metals.
17. The method of the preceding embodiment, wherein the transition metals comprise Ag, Pb, Sn, Zn, Al, Pd, Pt, Fe, Cu, Co, Ni, Al, or a combination thereof.
18. The method of any preceding embodiment, further comprising washing the refined precious metal with water, an aqueous solution, or a combination thereof.
19. The method of any preceding embodiment, further comprising pre-rinsing the precious metal prior to contacting with the refining solution, the pre-rinsing comprising contacting the precious metal with a dilute acidic solution;

contacting the acid-washed precious metal with an aqueous solution; and
contacting the aqueous-washed precious metal with a concentrated acid.

20. The method of the preceding embodiment, wherein the dilute acidic solution comprises HCl, HBr, HI, HNO₃, H₂SO₄, H₃PO₄, or a combination thereof.
- 5 21. The method of any preceding embodiment, wherein the concentrated acid comprises glacial acetic acid.
22. The method of any preceding embodiment, wherein the acid of the refining solution comprises HCl, HBr, HI, chlorous acid, chloric acid, bromous acid, bromic acid, iodous acid, iodine acid, perchloric acid, sulfuric acid, nitric acid, oxalic acid, phosphoric acid, an organic
10 acid, or combinations thereof.
23. The method of any preceding embodiment, wherein the acid of the refining solution comprises HCl, HBr, HI.
24. The method of any preceding embodiment, wherein the acid of the refining solution comprises HCl.
- 15 25. The method of any preceding embodiment, wherein the oxidant of the refining solution comprises HNO₃, H₂O₂, O₂, bubbled air, I₂, NaClO₂, NaClO₃, KClO₃, NH₄ClO₃, NaClO, K₂Cr₂O₇, KMnO₄, Ca(ClO)₂, Cl₂, CuCl₂, FeCl₃, CaO₂, sodium iodate, potassium iodate, manganese dioxide, perchloric acid, or combinations thereof.
26. The method of any preceding embodiment, wherein the oxidant of the refining solution
20 comprises KClO₃, NH₄ClO₃, NaClO₃.
27. The method of any preceding embodiment, wherein the oxidant of the refining solution comprises NaClO₃.
28. The method of any preceding embodiment, wherein the ligand source of the refining solution comprises a chloride salt.
- 25 29. The method of any preceding embodiment, wherein the ligand source of the refining solution comprises HCl, MgCl₂, AlCl₃, CaCl₂, or a combination thereof.
30. The method of any preceding embodiment, wherein the ligand source of the refining solution comprises MgCl₂.
31. The method of any preceding embodiment, wherein the partially water-miscible or
30 water-miscible solvent of the refining solution comprises glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, aqueous solutions thereof, or a combination thereof.
32. The method of any preceding embodiment, wherein the water-miscible solvent of the refining solution comprises glacial acetic acid, acetic acid, or a combination thereof. The

method of any preceding embodiment, wherein the water-miscible solvent of the refining solution comprises aqueous solutions of glacial acetic acid, acetic acid, or a combination thereof.

33. The method of any preceding embodiment, wherein the water-miscible solvent of the refining solution comprises glacial acetic acid, or aqueous solutions thereof.

34. The method of any preceding embodiment, wherein the precious metal comprises Au, Pt, Pd, Rh, Ru, Ir, Os, or a combination thereof.

35. The method of any preceding embodiment, wherein the precious metal comprises Au, Pd, Pt, Rh, or a combination thereof.

36. The method of any preceding embodiment, wherein the precious metal comprises Au.

37. The method of any preceding embodiment, wherein the refined precious metal has a purity of $\geq 99\%$, $\geq 99.9\%$, or 99.99% .

[00178] In one or more embodiments described herein, there is also provided:

1. A method of refining a precious metal sourced from jewelry, the method comprising adding the precious metal and an oxidant to a solution comprising an acid in a partially water-miscible or water-miscible solvent to form a leaching mixture; adding an additional dose of the oxidant to the leaching mixture after a first period of time; adding subsequent doses of the oxidant to the leaching mixture at time intervals after the first period of time; adding a final dose of the oxidant after the final time interval, and adding an additional dose of the acid to the leaching mixture; and forming a leached solution comprising a leached precious metal.

2. The method of embodiment 1, wherein the first period of time starts at the forming of the leaching mixture.

3. The method of any preceding embodiment, wherein the time intervals start at the adding of the first dose of the oxidant to the leaching mixture.

4. The method of any preceding embodiment, wherein the first period of time is about 1 to about 5 min; or about 1 to about 4 min; or about 1 to about 3 min.

5. The method of any preceding embodiment, wherein each of the time intervals is about 1 to about 5 min; or about 1 to about 4 min; or about 1 to about 3 min.

6. The method of any preceding embodiment, wherein adding the oxidant, adding the additional dose of the oxidant, and the subsequent doses of the oxidant comprises continuously dosing the oxidant into the refining solution over a period of time.

7. The method of any preceding embodiment, wherein continuously dosing the oxidant into the refining solution over a period of time comprises dosing the oxidant into the refining solution for the duration of leaching the precious metal into the refining solution; or dosing the oxidant into the refining solution for a period of time that is less than the duration of leaching the precious metal into the refining solution.
8. The method of any preceding embodiment, further comprising adding to the leached solution a second oxidant and a polyatomic salt to precipitate contaminants from the leached solution.
9. The method of any preceding embodiment, wherein the polyatomic salt comprises an ammonium salt.
10. The method of any preceding embodiment, wherein the polyatomic salt ammonium chloride, ammonium sulfate, ammonium nitrate, or combinations thereof.
11. The method of any preceding embodiment, further comprising adding a reductant to the leached solution to form a reducing solution; adding a first dose of a base to the reducing solution after a second period of time; optionally adding a second dose of the base after a third period of time; and precipitating the leached precious metal to form precipitated precious metal.
12. The method of any preceding embodiment, further comprising adding a reductant to the leached solution to form a reducing solution at a temperature above ambient; and precipitating the leached precious metal to form precipitated precious metal.
13. The method of any preceding embodiment, wherein the second period of time starts at the forming of the reducing solution.
14. The method of any preceding embodiment, wherein the third period of time is about 1 to about 10 min; or about 3 to about 10 min; or about 7 to about 10 min.
15. The method of the preceding embodiment, wherein the reductant comprises thiourea, sodium metabisulfite, sodium sulfite, or a combination.
16. The method of any preceding embodiment, further comprising contacting the precipitated precious metal with a rinse solution for dissolving additional contaminants, the rinse solution comprising a complexation reagent; and forming a refined precious metal.
17. The method of any preceding embodiment, wherein the contaminants comprise transition metals.
18. The method of the preceding embodiment, wherein the transition metals comprise late transition metals.

19. The method of the preceding embodiment, wherein the transition metals comprise Ag, Pb, Sn, Zn, Al, Pd, Pt, Fe, Cu, Co, Ni, Al, or a combination thereof.
20. The method of the preceding embodiment, wherein the transition metals comprise Ag, Pd, Pt, or a combination thereof.
- 5 21. The method of the preceding embodiment, wherein the transition metals comprise Pd, Pt, or a combination thereof.
22. The method of any preceding embodiment, further comprising washing the precipitated precious metal with water, an aqueous solution, or a combination thereof.
23. The method of any preceding embodiment, wherein the acid of the leaching mixture
10 comprises HCl, HBr, HI, chlorous acid, chloric acid, bromous acid, bromic acid, iodic acid, iodous acid, perchloric acid, sulfuric acid, nitric acid, oxalic acid, phosphoric acid, an organic acid, or combinations thereof.
24. The method of any preceding embodiment, wherein the acid of the leaching mixture comprises HCl, HBr, HI.
- 15 25. The method of any preceding embodiment, wherein the acid of the leaching mixture comprises HCl.
26. The method of any preceding embodiment, wherein the oxidant of the leaching mixture or the second oxidant comprises HNO_3 , H_2O_2 , O_2 , bubbled air, I_2 , NaClO_2 , NaClO_3 , KClO_3 , NH_4ClO_3 , NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , $\text{Ca}(\text{ClO})_2$, Cl_2 , CuCl_2 , FeCl_3 , CaO_2 , sodium iodate,
20 potassium iodate, manganese dioxide, perchloric acid, or combinations thereof.
27. The method of any preceding embodiment, wherein the oxidant or the second oxidant comprises KClO_3 , NH_4ClO_3 , NaClO_3 .
28. The method of any preceding embodiment, wherein the oxidant or the second oxidant comprises NaClO_3 .
- 25 29. The method of any preceding embodiment, wherein the partially water-miscible or water-miscible solvent of the leaching mixture comprises glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, or aqueous solutions thereof, or a combination thereof.
30. The method of any preceding embodiment, wherein the water-miscible solvent of the leaching mixture comprises glacial acetic acid, acetic acid, or a combination thereof. The
30 method of any preceding embodiment, wherein the water-miscible solvent of the leaching mixture comprises aqueous solutions of glacial acetic acid, acetic acid, or a combination thereof.

31. The method of any preceding embodiment, wherein the water-miscible solvent of the leaching mixture comprises glacial acetic acid, or aqueous solutions thereof.
32. The method of any preceding embodiment, wherein the precious metal comprises Au.
33. The method of any preceding embodiment, wherein the refined precious metal has a
5 purity of $\geq 99\%$, or $\geq 99.9\%$, or $\geq 99.9\%$.

[00179] System for Refining a Precious Metal

[00180] Also described herein is a system for refining a precious metal. The system may be used to carry out one or more of the methods of refining precious metal as described herein.
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[00181] System Components

[00182] With reference to Figure 1, and in an embodiment of the system described herein, the system comprises a leach reactor 1. The leach reactor 1 may be configured to conduct the leaching stage of the herein described refining method. The leach reactor may be
15 configured to receive one or more of the components that make up the refining solution of the refining method described herein. The leach reactor 1 may comprise a port for receiving precious metal for refining. Said port may be coupled to and/or in communication with a solids dosing system for providing the precious metal into the leach reactor 1 (not shown in Figure 1). The leach reactor 1 may be in fluid communication with a leach dosing system for dosing
20 the refining solution (otherwise referred to herein as a leaching mixture) into the leach reactor 1. The leach dosing system may comprise one or more reagent drums (which may otherwise be referred to as storage vessels, or storage tanks) in which the refining solution - or components of the refining solution - may be stored before use (noted in Figure 1 as R1, R2, R3). The one or more reagent drums may be in fluid communication with one or more reagent
25 pumps 2 for pumping the reagent into the leach reactor 1, the reagent pump being in fluid communication with leach reactor 1. The leach reactor may further comprise an agitator 13, for mixing the refining solution and precious metal once introduced therein.

[00183] The leach reactor 1 may also be in fluid communication with a first polishing filter system for filtering the leached solution and removing solids therefrom ahead of the
30 reduction stage of the herein described refining method. The first polishing filter system may comprise a transfer pump, such as transfer pump 4 of Figure 1; and one or more filters, such as filters 3* of Figure 1. The one or more filters may be upstream of the transfer pump, downstream of the transfer pump, or both. The one or more filters may be arranged in series

or in parallel. The first polishing filter system may comprise a filter system, such as filter system 20* of Figure 1 and Figure 2. The filter system may be coupled to the leach reactor 1, replacing the one or more filters.

[00184] The filters (for example, filters 3* or for filter system 20*) may comprise a pore size of about 1 to about 5 micron. The filters may comprise a filter composed a filter medium that is compatible with the refining solution, in that the filter medium may not react with, or break down in the presence of the refining solution. A suitable filter medium may be selected in view of the chemical and physical properties of the refining solution, such as pH, oxidizing potential, etc. and/or the temperatures to which the filter may be exposed. The filters may
5 comprise a filter composed of hydrophobic and/or inert filter mediums. The filters may comprise a filter medium composed of glass fibre media. The filters may comprise a filter medium composed of Polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polypropylene (PP), or a combination thereof. The one or more filters (for example filters 3*) may comprise cartridge filters, Buchner style filters, pocket leaf filters, bag filters, or a combination thereof.
10 The filters may comprise cartridge filters. The filters for the filter system (for example filters of filter system 20*) may comprise filters suitable for pressurized and/r vacuum filtration. The filters for the filter system (for example filters of filter system 20*) may comprise filters suitable for a candle filter setup.

[00185] The leach reactor 1 may also be in fluid communication with reduction reactor
20 6. The reduction reactor 6 may be configured to conduct the reduction stage of the herein described refining method. The reduction reactor may be configured to receive one or more of the components that make up a reducing mixture R6. The reducing mixture R6 may comprise the reductant of the refining method described herein. The reduction reactor 6 may be in fluid communication with a reducing dosing system for dosing the reducing mixture into the
25 reduction reactor 6. The reducing dosing system may comprise one or more reagent drums in which the reducing mixture R6 - or components of the reducing mixture - may be stored before use (noted in Figure 1 as R4, 9). The one or more reagent drums may be in fluid communication with one or more reagent pumps 5 or 10 for pumping the reagent into the reduction reactor 6, the reagent pumps being in fluid communication with reduction reactor 6.

30 [00186] The reduction reactor 6 may further comprise an agitator 14, for mixing the leached solution and reducing mixture once introduced therein. The reduction reactor 6 may further comprise an external heating source (not shown in Figure 1), such as a heating jacket,

heating blanket, heater, etc. to provide controlled heating during the reduction and/or rinsing stages of the herein described refining method, as needed.

[00187] The reduction reactor 6 may also be in fluid communication with a second polishing filter system for filtering - and therefore separating - the reduced precious metal from the leached solution of the herein described refining method. The second polishing filter system may comprise a transfer pump, such as transfer pump 7 of Figure 1; and a filter system, such as filter system 20* of Figure 1 and Figure 2. The second polishing filter system may comprise one or more filters, such as filters 3* of Figure 1. The one or more filters may be upstream of the transfer pump 7, downstream of the transfer pump 7, or both. The one or more filters may be arranged in series or in parallel.

[00188] The filters (for example, filters 3* or for filter system 20*) may comprise a pore size of about 1 to about 5 micron. The filters may comprise a filter composed a filter medium that is compatible with the leached solution, in that the filter medium may not react with, or break down in the presence of the leached solution. A suitable filter medium may be selected in view of the chemical and physical properties of the leached solution, such as pH, oxidizing potential, etc. and/or the temperatures to which the filter may be exposed. The filters may comprise a filter medium composed of hydrophobic and/or inert filter mediums. The filters may comprise a filter medium composed of glass fibre media. The filters may comprise a filter medium composed of Polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polypropylene (PP), or a combination thereof. The one or more filters (for example filters 3*) may comprise cartridge filters, Buchner style filters, pocket leaf filters, bag filters, or a combination thereof. The filters may comprise cartridge filters. The filters for the filter system (for example filters of filter system 20*) may comprise filters suitable for pressurized and/or vacuum filtration. The filters for the filter system (for example filters of filter system 20*) may comprise filters suitable for a candle filter setup.

[00189] The reduction reactor 6 may also be in fluid communication with reagent make-up reactor 9. Reagent make-up reactor 9 may make up part of the reducing dosing system. The reagent make-up reactor 9 may be configured to provide and/or form the reducing mixture R6 described herein. The reagent make-up reactor 9 may be configured to receive one or more of the components that make up the reducing mixture. Reagent make-up reactor 9 may comprise a port for receiving the reductant (noted in Figure 1 as R5). Said port may be coupled to and/or in communication with a solids dosing system for providing the reductant into the reagent make-up reactor 9 (not shown in Figure 1). The reagent make-up reactor 9 may be in

fluid communication with an aqueous dosing system for dosing water or aqueous solution into the reagent make-up reactor 9, as part of forming the reducing mixture. The aqueous dosing system may comprise one or more drums in which the water or aqueous solution may be stored before use (noted in Figure 1 as R4). The one or more reagent drums may be in fluid communication with one or more pumps 8 for pumping the water or aqueous solution into reagent make-up reactor 9, the pump being in fluid communication with reagent make-up reactor 9.

[00190] The reagent make-up reactor 9 may further comprise an agitator 15, for mixing the components of the reducing mixture once introduced therein. The reagent make-up reactor 9 may further comprise an external heating source (not shown in Figure 1), such as a heating jacket, heating blanket, heater, etc. to provide heating during formation of the reducing mixture and/or rinsing stages of the herein described refining method, as needed. The reduction reactor 6 may also be in fluid communication with a spent leached solution storage tank, for example via filter 11 of Figure 1, and/or may be in fluid communication with aqueous waste storage tank, for example via filter 12 of Figure 1.

[00191] The reagent make-up reactor 9 may also be in fluid communication with a filter system for filtering the reducing mixture R6 prior to use in the reduction reactor 6. The filter system may comprise one or more filters, such as filters 13 of Figure 1. The one or more filters may be upstream of the transfer pump 10, downstream of the transfer pump 10, or both. The one or more filters may be arranged in series or in parallel. The filter system may comprise a transfer pump, such as transfer pump 10 of Figure 1; and a filter system, such as filter system 20* of Figure 1 and Figure 2. The filter system may be coupled to the make-up reactor 9, replacing the one or more filters.

[00192] The filters (for example, filters 3* or for filter system 20*) may comprise a pore size of about 1 to about 5 micron. The filters may comprise a filter composed a filter medium that is compatible with the reducing mixture, in that the filter medium may not react with, or break down in the presence of the reducing mixture. A suitable filter medium may be selected in view of the chemical and physical properties of the reducing mixture, such as pH, oxidizing potential, etc. and/or the temperatures to which the filter may be exposed. The filters may comprise a filter medium composed of hydrophobic and/or inert filter mediums. The filters may comprise a filter medium composed of glass fibre media. The filters may comprise a filter medium composed of Polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polypropylene (PP), or a combination thereof. The one or more filters (for example filters 3*)

may comprise cartridge filters, Buchner style filters, pocket leaf filters, bag filters, or a combination thereof. The filters may comprise cartridge filters. The filters for the filter system (for example filters of filter system 20*) may comprise filters suitable for pressurized and/or vacuum filtration. The filters for the filter system (for example filters of filter system 20*) may
5 comprise filters suitable for a candle filter setup.

[00193] If or when reagents are commonly used across more than one reactor of the system, there may be one reagent drum and pump for that reagent, and diverting valves may be used to direct the reagent to the appropriate reactor (shown in Figure 1; for example, see symbol ).

10 **[00194]** The transfer pumps described herein may be diaphragm pumps. Diaphragm pumps may be used to reduce, prevent, or minimize line losses of pregnant leach solution comprising precious metal (otherwise referred to herein as leached solution). Diaphragm pumps may be used due to: their chemical compatibility; ability to handle solids; ability to control discharge pressure based on input air pressure; and/or ability to reduce, prevent, or
15 minimize dead space in system. The reagent pumps described herein may be peristaltic pumps. Peristaltic pumps may be used due to their ability to offer fine dosing control of input chemicals.

[00195] As described above, the reduction reactor 6 may comprise a filter system 20 such that reduction and/or filtration may occur in one vessel. This combination of reactor and
20 filter system may reduce precious metal losses on reactor and/or pump walls and lines. As described above, the first polishing filter system may remove solids and/or impurities from the leached solution before it enters the reduction reactor 6. Said solids may comprise silver, silver salts, non-metal impurities, such as plastics or organics, etc. This may facilitate achieving at least 999s, if not 9999s selectivity for the final, isolated precious metal. As described above,
25 the reactors further comprises an agitator. The agitator may be a vibratory agitator. Such vibratory agitators may impart low shear in liquid media, which may facilitate maintaining gaseous oxidants remain in solution, thereby supporting faster leaching kinetics. Further, vibratory agitators may not be limited to reactor shape, and may reduce or prevent dead zones in reactor (see Figure 4). Vibratory agitators may also suspend dense metal in a reactor, which
30 may facilitate reaction kinetics.

[00196] The system as described herein may further comprise one or more kidney loops. A kidney loop comprises a recycle loop back to a reactor/tank that a solution is coming

out of. The system as described herein may further comprise one or more kidney loops at the leaching stage. The system as described herein may further comprise one or more kidney loops at the end of the reduction stage. The system as described herein may further comprise one or more kidney loops at the end of the reduction stage to recirculate leached solution that
5 may have passed through filter system 20 before the therein leached precious metal could be reduced, so that said leached solution could continue to be contacted with the reducing mixture to reduce the therein leached precious metal; and thus potentially improve yield of reduced precious metal. Further, kidney looping may allow for a cake of reduced precious metal to build up without sending the filtrate to a waste tank. Thus, if there are precious fines that pass
10 through the filter system, it may be recovered in the precious metal cake that builds up during the kidney loop stage.

[00197] If the absence of kidney loop, some precious metal loss may be observed if leached solution that still comprises leached precious metal bypasses the filter system and goes into a waste drum, such as a spent leached solution storage tank. If leached precious
15 metal were to be lost in this way, it may not be captured by the polishing filter systems downstream of the reduction reactor, as said leached precious metal may not have enough time to react with the reducing mixture to be reduced and precipitate. If the absence of kidney loop, some precious metal loss may be observed if - at the beginning of the reduced precious metal filtration - the reduced precious metal cake is not fully formed which may result in fine
20 precious metal particles not being effectively filtered. The fine precious may be captured in a polishing filter, but that may require further manual work to recover.

[00198] The filters of the system described herein may comprise filter media having high purity, which may prevent shedding of the filter media and thus facilitate refining a precious metal to a high purity.

[00199] With further reference to Figure 2, the filter system 20 as described above comprises a filter base 24 for coupling the filter system to a reactor, a perforated plate 23 which may be optionally present and may support filter medium 22, a filter medium 22 which is configured to collect solids in solutions that are filtered therethrough, and a centering ring 21 for providing a liquid-tight seal. The filter medium may comprise a frit. The filter medium may
30 comprise a frit, one or more filter papers, or a combination thereof.

[00200] Refining System as Described Herein

[00201] At least in view of the forgoing, there is provided herein a system for refining a precious metal, the system comprising: a leach reactor, the leach reactor having a first agitator and a first port for dosing a precious metal into the leach reactor, the leach reactor being in fluid communication with a leach dosing system for dosing a refining solution into the leach reactor; and a reduction reactor in fluid communication with the leach reactor, the reduction reactor having a second agitator, and being in fluid communication with a reducing dosing system for dosing a reducing mixture into the reduction reactor, and a rinsing system for dosing a rinse solution into the reduction reactor; the precious metal and refining solution being dosed into the leach reactor and agitated to leach the precious metal into the refining solution and form a leached solution comprising a leached precious metal; the leached solution being transferred to the reduction reactor; the reducing mixture being dosed into the reduction reactor; and being agitated to reduce the precious metal and form precipitated precious metal.

[00202] The system may further comprise a first polishing filter system in fluid communication with the leach reactor, the first polishing filter system comprising a filter in fluid communication with the leach reactor and a first transfer pump, the transfer pump being in fluid communication with the reduction reactor; wherein: the leached solution being transferred to the reduction reactor comprises filtering the leached solution through the polishing filter system to remove insoluble impurities from the leached solution.

[00203] The system may further comprise a first polishing filter system coupled to leach reactor, the first polishing filter system comprising a filter system coupled to the leach reactor and a first transfer pump, the transfer pump being in fluid communication with the reduction reactor; wherein the leached solution being transferred to the reduction reactor comprises filtering the leached solution through the polishing filter system to remove insoluble impurities from the leached solution.

[00204] The system may further comprise a second polishing filter system coupled to the reduction reactor, the second polishing filter system comprising a filter system coupled to the reduction reactor in fluid communication with a second transfer pump, the transfer pump being in fluid communication with the reduction reactor; wherein reducing the precious metal and forming precipitated precious metal comprises forming a spent leached solution and precipitated precious metal mixture, and filtering the mixture through the second polishing filter system to remove the precipitated precious metal from the mixture.

[00205] The system may further comprise a second polishing filter in fluid communication with the reduction reactor, the second polishing filter system comprising a filter in fluid communication with reduction reactor and a second transfer pump, the transfer pump being in fluid communication with the reduction reactor; wherein reducing the precious metal and forming precipitated precious metal comprises forming a spent leached solution and precipitated precious metal mixture, and filtering the mixture through the second polishing filter system to remove the precipitated precious metal from the mixture. Filtering the mixture through the second polishing filter system to remove the precipitated precious metal from the mixture may comprise recycling the filtered spent leached solution back to the reduction reactor.

[00206] The filter system may comprises a base to couple to the reactor; and a filter medium coupled to the base. The filter medium may comprise a frit and/or optionally least one filter paper. The frit and/or optionally least one filter paper may comprise a polyalkylene, a polyfluorinated polymer, or a combination thereof. The frit may comprise a about 1 micron to about 5 micron rating. The at least one filter paper may comprise a about 0.45 to about 3 micron rating.

[00207] The leach dosing system may comprise a first reagent drum in fluid communication with a first reagent pump, the first reagent drum comprising the refining solution and the first reagent pump in fluid communication with the leach reactor. In embodiments where the refining solution comprises a solvent, an acid, and an oxidant, and the leach dosing system may comprise a leach solvent drum in fluid communication with a leach solvent pump, the leach solvent pump being in fluid communication with the leach reactor; a leach acid drum in fluid communication with a leach acid pump, the leach acid pump being in fluid communication with the leach reactor; and a leach oxidant drum in fluid communication with a leach oxidant pump, the leach oxidant pump being in fluid communication with the leach reactor; wherein: the solvent, acid, and oxidant are separately dosed into the leach reactor to form the refining in the leach reactor.

[00208] The reducing dosing system may comprise a second reagent drum in fluid communication with a second reagent pump, the second reagent drum comprising the reducing mixture and the second pump being in fluid communication with the reduction reactor. In embodiments wherein the reducing mixture comprises a reductant, optionally in solution, the reducing dosing system may comprise: a reagent make-up reactor, the reagent make-up reactor having an agitator and a first port for dosing the reductant into the mixing reactor, the

reagent make-up reactor being in fluid communication with the reduction reactor; and an optional solution drum in fluid communication with an optional solution pump, the solution pump being in fluid communication with the reagent make-up reactor; wherein: the reductant and optional solution are dosed into the reagent make-up reactor and agitated to form the reducing mixture. In embodiments wherein the reducing mixture comprises a reductant in solution, the system may comprise the solution drum and pump. In embodiments wherein the reducing mixture comprises a reductant in aqueous solution, the solution drum and pump comprise an aqueous solution drum and an aqueous solution pump.

[00209] In embodiments wherein the rinse solution comprises a rinse acid and a rinse complexing agent, the rinsing system may comprises: a third reagent drum in fluid communication with a third reagent pump, the third reagent drum comprising a rinse acid and the third pump being in fluid communication with the reduction reactor; and a fourth reagent drum in fluid communication with a fourth reagent pump, the fourth reagent drum comprising a rinse complexing agent and the fourth pump being in fluid communication with the reduction reactor; wherein: rinse complexing agent and rinse acid are dosed into the reduction reactor to form the rinse solution, and the rinse solution is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal.

[00210] The fourth reagent drum comprising the rinse complexing agent in fluid communication with the fourth reagent pump, the fourth reagent drum and pump being in fluid communication with the reducing reactor may comprise the reducing dosing system, wherein the solution drum and pump comprise an aqueous solution drum and an aqueous solution pump, and aqueous solution is dosed into the reduction reactor, the reductant is dosed into the reduction reactor, and the rinse acid is dosed into the reduction reactor, to form the rinse solution, and the rinse solution is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal.

[00211] The system may further comprise dosing additional aqueous solution into the reduction reactor and flowing through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal.

[00212] The third reagent drum comprising the rinse acid in fluid communication with the third reagent pump, the third reagent drum and pump being in fluid communication with the reduction reactor may comprise the leach acid drum in fluid communication with a leach acid

pump, the leach acid pump being diverted to be in fluid communication with the reduction reactor.

[00213] In embodiments wherein the rinse solution comprises a rinse acid and a rinse complexing agent, the rinse complexing agent may comprise the reducing mixture, and the rinsing system may comprise: a third reagent drum in fluid communication with a third reagent pump, the third reagent drum comprising the rinse acid and the third pump being in fluid communication with the reduction reactor; a fourth reagent drum in fluid communication with a fourth reagent pump, the fourth reagent drum comprising an aqueous solution and the forth pump being in fluid communication with the reducing reactor; and the reducing dosing system; wherein: the aqueous solution is dosed into the reduction reactor, the reducing mixture is dosed into the reduction reactor, and the rinse acid is dosed into the reduction reactor, to form the rinse solution, and the rinse solution is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal; and optionally an additional dose of aqueous solution is dosed into the reduction reactor and is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal.

[00214] In one or more embodiments of the present disclosure, the system described herein may be a pilot scale hydrometallurgical gold refinery system. It may process raw (unrefined) gold powder into high purity (>99.99% grade) gold powder. A standard batch size may be approximately 500g of raw gold powder. A total reaction duration per batch may be approximately 70 minutes. The system may be housed inside of a spill containment berm (for example, a 12ft x 12ft (3.7m x 3.7m) containment berm) . As part of the refining process, hazardous gas mixtures may be generated - and as such, the system may be isolated from the environment via one or more fume hoods (process) and a fume cabinet (reagent storage).

[00215] The system for refining as described herein may further comprise the following:

- i) Air Operated Double Diaphragm pumps for transferring pregnant leach solution (otherwise referred to as leached solution) from leach reactor to reduction reactor – which may be chosen due to chemical compatibility; ability to handle solids; ability to control discharge pressure based on input air pressure; and/or ability to reduce, prevent, or minimize dead space in system. For example, see Figure 1, pumps 4 and 7.

(a) May also be used for transfer of Spent solution (post reduction; otherwise

referred to as leached solution from which the reduced precious metal was precipitated and removed) and waste rinse solutions from Reduction reactor.

- 5 ii) Peristaltic pumps for chemical dosing into leach reactor or chemical reactor – which may be chosen due to ability to have fine dosing control of input chemicals. For example, see Figure 1, pumps 2, 5, 8 and 10.
- iii) Glass reactors for Leach reactor and Reduction reactor, which may be chosen for chemical compatibility and/or visibility to reactions.
- 10 iv) Specific types/models of glass reactors may be chosen to minimize dead space. For example, see Figure 1, reactors 1, 6, and 9. In Leach reactor 1, minimizing dead space may facilitate the ability to leach a sufficient amount, most, or all input precious metal.
- v) In Leach reactor 1, a vibratory agitator (Fundamix) may be used to: maintain suspension of heavy precious metal particles within the solution; to allow efficient leaching, for example in a short timeframe (on the order of 10 minutes); and/or impart low shear in
15 liquid media, ensuring gaseous oxidant remains in solution, thereby facilitating fast kinetics of reaction.
- vi) Pressure relief valve installed on the reactors, which may be chosen with chemically compatible materials as well as appropriate setpoint to maintain reagent levels in solution to aid Leaching efficiency.
- 20 vii) For Reduction reactor 6, a filter system (for example, see Figure 2) may be chosen for ability to execute reduction reaction within the reactor while reducing, preventing, or minimizing passing of pregnant leach/unreduced precious metal within the reactor until reduction is complete. Specific filter materials/pore size/layering may be chosen to reduce, prevent, or minimize solid precious metal passing through and/or to allow efficient
25 filtration/flow. For example, partially hydrophobic and/or chemically inert filter mediums may be used to stop/slow passive movement of solution through the filter, but also allow efficient filtering with a vacuum. For example, see Working Example 7.
- viii) Plastic components (for example, tubing, fittings, valves, etc.), for which polyvinylidene fluoride (PVDF) and/or Polytetrafluoroethylene (PTFE) may be chosen for chemical
30 compatibility and pressure/vacuum ratings. A minimum amount of tubing & fittings may be used to reduce, prevent, or minimize amount of precious metal containing solution that could become trapped between reactors, etc.

- ix) Air operated diaphragm valves – chosen for chemical compatibility and ability to handle solids, as well as reducing, preventing, or minimizing dead space in the system (i.e. left over gold containing solution) These may be located where flow control and/or flow redirection are necessary. Some are shown in Figure 1 between pumps and filters.
- 5 x) PTFE canister filters and cartridges may be used in the first polishing filter system for: offered pressure and temperature ratings, chemical compatibility, ability to remove fine particles when transferring to reduction reactor; and/or ability to capture any solid precious metal remaining in spent leached solution. For example, Figure 1, filters 3*, 11, and 12 may be polishing cartridge filters.
- 10 xi) Heating blanket on Reduction reactor 6 may be used to maintain minimum temperature for reduction of precious metal and level of purity.
- xii) Compressors may be used to move air or other gaseous substances, as needed. For example, such compressors may be in communication with leach reactor 1 and may be used to purge reactor 1 of any gas produced, for safe handling, for maintenance etc.
- 15 xiii) Chemicals and reactor systems may be stored within a ventilated space with filtering and/or scrubbing mediums rated for any expected gaseous byproducts.
- xiv) Pneumatic control system may be used to allow for external control of flow path to mitigate operator exposure to hazardous chemicals.
- 20 **[00216]** In one or more embodiments of the present disclosure, the refining method as described herein may be conducted within the system described herein as follows:
- [00217] Feedstock preparation:**
- [00218]** Gold feedstock may be sieved before being added to obtain <250 um particle
25 size. The system described herein may manage larger particles, but more time and/or more chemicals may be needed.
- [00219] Thiourea solution preparation:**
- [00220]** A saturated solution (0.142 g/mL) of *thiourea* is prepared in a 20 L jacketed reactor by pumping in 2500 mL *water* into it, and then adding 355 g of *thiourea*. This solution
30 is stirred with an overhead agitator for 60 minutes at 30°C until the *thiourea* solid dissolves, and then the solution is kept at this temperature until needed in the refining process to ensure that solids do not drop out.

[00221] In one or more embodiments of the refining method and refining system described herein, this thiourea solution preparation section describes an example of preparing the reducing mixture as described herein, in the reagent make-up reactor as described herein.

[00222] **Leach Preparation:**

5 [00223] A refining solution was prepared in a 5 L reactor by pumping in 338 mL *water*, followed by 628 mL *glacial acetic acid*, and then 924 mL concentrate *HCl*. The overhead agitator in this reactor is turned on to homogenize this mixture. Upon mixing, 420 g of powdered gold is added into the reactor. Once the powdered gold is well combined in the solution, dosing of NaClO_3 solution (40% w/w) begins. This solution is dosed at 42 mL/min for 5 minutes, 10 totalling an added volume of 210 mL. The leach reaction takes place over about 10 minutes until no visible gold remains in solution and then the solution is sampled for ICP-OES analysis from the top through a sampling tube. Following this sample, the gold-containing leached solution is pumped through a cartridge filter into a 5 L reduction reactor equipped with a heating belt. 250 mL *glacial acetic acid* is dosed into the original leach reactor and pumped through 15 the lines and cartridge filter to bring over any remaining leach solution that is still held in the lines.

[00224] In one or more embodiments of the refining method and refining system described herein, this leach preparation section describes an example of preparing the refining solution as described herein in the leach reactor via the leach dosing system as described 20 herein to conduct the leaching and form the leached solution comprising leached precious metal as described herein.

[00225] In one or more embodiments of the refining method and refining system described herein, this leach preparation section describes an example of filtering the leached solution through the first polishing filter system as described herein for filtering the leached 25 solution and removing solids, and then transferring said filtered, leached solution to the reduction reactor as described herein.

[00226] **Gold Reduction:**

[00227] The gold-containing leached solution that was pumped over to the reduction reactor is stirred using an overhead agitator, and then 592 mL of the pre-prepared saturated 30 *thiourea* solution is dosed into the reactor. Once the *thiourea* solution was added in, the heating belt is set to about 63°C and the whole solution is agitated at this temperature for 60 minutes. After 60 minutes, agitation is stopped, the gold allowed to settle, and the leached solution is sampled for ICP-OES analysis from the top using a sampling tube, and then the leached

solution is filtered through the bottom filter system in the reduction reactor, kidney looped back through the reactor for about 10 minutes and then fully filtered through the bottom filter system, a polishing cartridge filter, and then pumped into a container for storage or disposal. Once the reduction filtrate is removed, all that remains in the reactor is refined powdered gold. The heating belt is turned off.

[00228] In one or more embodiments of the refining method and refining system described herein, this gold reduction section describes an example of reducing the leached precious metal in the presence of the reducing mixture as described herein in the reduction reactor, by dosing in the reducing mixture from the reagent make-up reactor as described herein as part of the reducing dosing system as described herein.

[00229] In one or more embodiments of the refining method and refining system described herein, this gold reduction section describes an example of filtering the leached solution and reduced precious metal mixture through the second polishing filter system of the reduction reactor as described herein for separating the reduced precious metal from the leached solution.

[00230] To this reactor, 2.1 L of *water* is pumped in, and agitation started, to stir and rinse the gold for 2 minutes. After 2 minutes, this *water* rinse is filtered out into an aqueous waste container. Next, the *thiourea* and *HCl* rinse is prepared in the reduction reactor on top of the gold by pumping in 883 mL *water*, starting agitation, then pumping in 1129 mL pre-prepared saturated *thiourea* solution, followed by 88 mL of concentrated *HCl*. This rinse and the gold are agitated for about 10 minutes. After 10 minutes, agitation is stopped, the gold allowed to settle, the rinse sampled from the top for ICP-OES analysis, and then the rinse is filtered out into the aqueous waste container. Once more, 2.1 L *water* is pumped into the reactor, the agitation turned on, the gold rinsed one final time for 2 minutes, and then the agitation is turned off, the gold allowed to settle, and the *water* rinse pumped and filtered out into the aqueous waste container.

[00231] In one or more embodiments of the refining method and refining system described herein, this gold reduction section describes an example of rinsing the reduced, precipitated precious metal using by dosing the rinse solution as described herein into the reduction reactor, via the rinse system as described herein, with agitation as described herein.

[00232] The filter system of the reduction reactor is removable, and so this is unlatched and the gold cake removed from the reactor and placed onto a hot plate to dry. Once dry, the

gold is removed from the filter into a clean container, mixed well, and then 0.5 g of the gold is removed for a purity analysis by digesting it in 20 mL of reverse-aqua regia.

[00233] In one or more embodiments of the present disclosure, when the refining method described herein is conducted within the system described herein, the following may be observed:

- i) Ability to maintain suspension of heavy precious metal particulates within the leach reactor until completion of leach.
- ii) Ability to filter out remaining or precipitated solids from leached solution when transferring to reduction reactor.
- iii) Ability to maintain required temperature in reduction reactor during process to facilitate recovery of solid precious metal.
- iv) Ability to separate out reduced precious metal from spent leached solution and/or rinse solutions from reduction reactor, while also having efficient filtering (for example, reducing, preventing, or minimizing time to filter)
- v) Use of two separate reactors for leach and reduction may prevent and/or reduce impurities from impacting the reduction stage.
- vi) Agitation using a vibratory agitator in leach reactor may reduce or eliminate dead space in reactor.
- vii) Transfer pumps that may be configured to run dry to reduce, prevent, or minimize precious metal leach solution losses in lines.
- viii) Reducing or Minimizing head space in leach reactor may facilitate maintaining gaseous oxidant at a concentration in headspace that help drive kinetics of precious metal dissolution reaction.
- ix) Using a rinse system facilitated washing away trace impurities from the solid precious metal reduced from the leached solution.
- x) Using a polishing filter system on leach reactor discharge facilitates removing solid impurities from entering the reduction stage.

[00234] To gain a better understanding of the invention described herein, the following examples are set forth. It should be understood that these examples are for illustrative purposes only. Therefore, they should not limit the scope of this invention in anyway.

5 [00235] **EXAMPLES**

[00236] **Example 1 - Refining Precious Metals**

[00237] Refining is the process in which impurities are removed from precious metals, such as gold, resulting in gold with purity of at least 99%, or at least 99.9%, or 99.99%, also known as fine gold or 9999. In 9999 gold, it is expected to see less than 100 mg/kg of
10 impurities.

[00238] Currently, industry standard is to refine precious metals, such as gold using a combination of the Miller and Wohlwill processes. In the Miller process, gold of 95% purity and below is melted down and chlorine gas is bubbled through the molten metal. Impurities bind to the chlorine and are collected as slag, leaving 99.5% pure gold to be poured into an anode
15 mold to continue to the Wohlwill process. In the Wohlwill process, the gold is purified electrolytically in a bath of chloroauric acid.

[00239] Both the smelting process and the shipment of precious metal, such as gold to and from the smelting facilities incur a significant cost. Thus, being able to achieve 9999 purity at a leaching facility may reduce the cost of refining.

20 [00240] Described herein is a procedure involving a hydrometallurgical process in which impure gold (e.g., from jewelry and/or e-waste) are refined. At a laboratory scale, it was found that the refining process could be performed in under two hours using readily available glassware and reagents.

[00241] **MATERIALS**

25 [00242] Chemicals

[00243] All chemicals were purchased as reagent grade and used without further purification. Acids, solvents, salts, reducing agents, and oxidants including ultra-pure 37% HCl, ultra-pure 70% nitric acid, ammonium chloride, magnesium chloride, ascorbic acid, iron (III) chloride, thiourea, sodium metabisulfite, and sodium chlorate were purchased from VWR and
30 used as received. Glacial acetic acid was purchased in bulk from Univar.

[00244] Equipment

[00245] All glassware, weigh boats, scoopulas, pipettes, and micropipette tips were taken from new stock and were both cleaned and stored separately from the rest of the

laboratory equipment. Other necessary equipment used included magnetic stir plates, Büchner funnels and flasks, and appropriate filter papers. Analysis was carried out using Thermo Scientific iCAP PRO XP Duo instrument, using ICP grade standards from Fisher Scientific.

[00246] ANALYSIS

5 **[00247] ICP-OES**

[00248] Analysis was carried out using a Thermo Scientific iCAP PRO XP Duo (ICP-OES) instrument. Standards and samples are diluted in approx. 3% HNO₃ solution using reverse-osmosis water to match the matrix of each sample being analyzed to the standards. Argon was used as both the cooling gas and carrier gas for this instrument. Quality control samples were analyzed approximately every 10-20 samples to observe possible instrument drift and to ensure proper calibration.

[00249] FEEDSTOCK

[00250] Precious metals subjected to the herein described refining method may be extracted from any substance comprising precious metal, using any method suitable for doing so. In the present example, gold powder was obtained from two sources: e-waste and jewelry.

15 **[00251]** In the case of e-waste, gold was leached using two methods: for Experiment 1, a leaching process involving a pilot-scale reactor was used, with the substance comprising precious metal comprising a combination of RAM fingers and centre-punched black CPUs (see Summary Tables 1A-H); and for Experiment 2, a leaching process involving a pilot-scale powder reactor was used, with the substance comprising precious metal comprising IC-chip concentrate (see Summary Tables 2A-H). For Experiment 3, impure gold collected from jewelry was used (see Summary Tables 3A-H).

[00252] CHEMICAL PROCESSING

[00253] General Chemical Processing Procedure

25 **[00254]** Gold powder obtained from various sources was first rinsed with a selection of solutions, as described below. After rinsing, the gold powder was leached using a refining solution, otherwise referred to herein as a lixiviant, containing appropriate amounts of solvent, oxidant, acid, and ligand source, stirring at 700 rpm at standard ambient temperature and pressure conditions for twenty minutes. The lixiviant solution was recharged regularly as needed, by adding in any one or more of the acid, oxidant, or ligand source. After completion of the leach, the solution was filtered to separate the solid by-product and the filtrate was analyzed by ICP-OES. Based on the gold content, a solution containing the appropriate amount of reducing agent was added to the filtrate and the reaction proceeded until the filtrate

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no longer contained gold, as analyzed by ICP-OES. The solution was then filtered to collect the gold, and then the solid powder was rinsed with a selection of solutions, as described below, before drying. After drying, 0.1 g of the solid was treated with 20 mL of reverse aqua regia (three volumetric parts of conc. HNO_3 and one volumetric part of conc. HCl) for 20 minutes to complete dissolution of the solid. This solution was then diluted and analyzed by ICP-OES to determine purity.

[00255] Selected Example of Chemical Processing

[00256] The processing began with a pre-rinsing step. 150 mL of a 0.5 mol/L HCl solution was prepared in a 400 mL beaker fitted with an appropriately sized stir bar. Subsequently, 30 g of gold extracted from E-waste was added to this beaker and rinsed with stirring at approx. 700 rpm in this solution for 10 minutes. After 10 minutes, the stirring was stopped, and the gold was allowed to settle. Once settled, an aliquot was removed for analysis by ICP-OES and then the solution was decanted. The gold was then washed with 150 mL and 60 mL of distilled water and glacial acetic acid respectively. After each rinse, the solution was allowed to settle, sampled for analysis by ICP-OES, and decanted.

[00257] A refining solution was prepared in another 400 mL beaker by mixing 90 mL glacial acetic acid as a water-miscible organic solvent, 60 mL concentrated HCl as an acid, and 7.5 g MgCl_2 as an additional ligand source. After allowing the MgCl_2 to slightly dissolve, an initial volume of 5 mL NaClO_3 solution (100% w/w) as an oxidant was slowly added to the solution, followed immediately by all the previously rinsed gold. The refining solution was dosed with another 5 mL NaClO_3 solution at 3 and 6 minutes before allowing the reaction to proceed for 15 minutes to leach all the gold. Though it was noted that all of the oxidant could have been added at once, it was found that dosing the oxidant into the refining solution at specific time intervals improves leaching efficiency.

[00258] Once leaching the gold into the refining solution was completed, the so formed leach solution was vacuum filtered, and the filtrate collected in a third 400 mL beaker with a stir bar. An aliquot was removed for analysis by ICP-OES. To this beaker, a solution of 60 g sodium metabisulfite as reducing agent in 91.9 mL water was slowly added. Once the entire volume of this solution was added, the reaction was allowed to proceed for 20 minutes. After 20 minutes, an aliquot was removed and centrifuged such that the filtrate could be sampled for analysis by ICP-OES. Once the analysis of this filtrate reads <10 mg/L gold in solution, it was filtered by vacuum. If there was still >10 mg/L gold in solution, the reaction was allowed to proceed and sampled every 10 minutes until the filtrate reads <10 mg/L gold.

[00259] After the filtration of the gold solution, the vacuum flask was replaced and 150 mL of *water* was poured over the gold cake, and approx. 10 mL *water* was used to rinse out the reaction vessel. Once the filtration was complete, a second measure of 150 mL of *water* was poured over the cake. In parallel, 150 mL of a 0.5 M *HCl* and 1 M *thiourea* solution was prepared in a 400 mL beaker with a stir bar, to be used as a rinse solution. The rinse solution may remove metal contaminants, such as Ag, Zn, Al. Once the *thiourea* was dissolved, the gold was removed from the Büchner funnel and added to the beaker to be rinsed in this solution for 10 minutes. After 10 minutes, the stirring was stopped, and the gold was allowed to settle. Once settled, an aliquot was removed for analysis by ICP-OES and then the solution was decanted. The gold was then washed with 150 mL of *water*, twice. After each rinse, the solution was allowed to settle, sampled for analysis by ICP-OES, and decanted.

[00260] The gold was briefly rinsed with methanol to expedite drying. This methanol was decanted and then the gold dried on a hot plate at 110°C. Upon drying, 0.1 g of the gold was removed for digestion with reverse aqua regia for 20 minutes, allowed to degas and then dilutions of 2, 10 and 1000 times were prepared for analysis by ICP-OES. The results of this analysis were used to calculate the purity of the gold using the following Equation 1:

$$Purity \% = \left(\frac{1,000,000 - SUM \left(Impurities \text{ in } \frac{mg}{kg} \right)}{1,000,000} \right) * 100\% \quad (1)$$

20 [00261] RESULTS & DISCUSSION

[00262] E-Waste Gold: Experiment 1

[00263] The results of the ICP-OES analysis were used to track the removal of contaminant metals, otherwise referred to herein as metal impurities, from the gold solid or gold-containing lixiviant solution. The results in this first section are those that apply directly to the experiment described above. Table 1 shows the impurities that remained in various rinse or filtrate solutions, meaning that these processes removed these metals. The values listed in the table below are in solution, and so are listed in mg/L - as compared to the metal impurities present in the solid gold in Table 2 which are listed in mg/kg. Thus, the values in Tables 1 and 2 may not be directly compared. The initial 0.5 mol/L *HCl* solution rinse (pre-rinse) that the gold underwent prior to leaching with the refining solution was responsible for removing a large amount of Pb, and lower but still significant quantities of Sn, Fe and Al. The gold was then

leached, filtered, and precipitated, and so the metals remaining in the post-reduction filtrate were considered removed impurities. These metals included Sn, Ag, Cu, Fe, Zn and Al. Finally, the precipitated gold was rinsed using a rinsing solution of *thiourea* and *HCl* and this solution shows removal of more Ag and Zn.

5

[00264] **Table 1:** Summary of the impurities removed from the Experiment 1 gold in the key steps of the refining process in milligrams per litre of solution.

Sample	Surface E-Waste Refining - Metals in Solution (mg/L)									
	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Co	Al
HCl Rinse	0.3	0.1	24.7	204.2	0.9	4.0	28.1	1.7	0.2	29.0
Post-Reduction Filtrate	0.3	0.4	11.5	0.5	7.1	8.5	4.9	6.4	0.7	7.9
Thiourea Rinse	0.0	0.1	0.0	0.2	23.4	0.3	0.0	3.5	0.0	0.1

10 **[00265]** Taking into consideration the impurities that have been removed, Table 2 below shows the summary of the metal impurities found in the Experiment 1 feed gold before the leach and is followed by the metal impurities found in the refined gold. As evidenced by the values shown below, the rinse and leach processes were able to remove 100% of the Pt, Pd, Sn, Pb, Cu, Fe, Zn, and Co. The impurities that remain are Ag and Al, totalling to 33 mg/kg.

15 This corresponds to a purity of 99.997%.

[00266] **Table 2:** Summary of the metal impurities found in gold solid before and after the refining process in milligrams per kilogram, carried out on e-waste gold obtained from Experiment 1.

		Surface E-Waste - Impurities Present in Gold Solid (mg/kg)									
Sample	Purity (%)	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Co	Al
Initial	99.598%	15	17	457	1371	985	170	268	369	10	349
Refined	99.997%	0	0	0	0	21	0	0	0	0	12

20

[00267] Also see Summary Tables 1A-H.

[00268] E-Waste Gold: Experiment 2

25 **[00269]** The results in this section are from an experiment in which the exact same process outlined in the section “Selected Example of Chemical Processing” was used on feed gold obtained from RAM and IC Chip powder concentrate. Table 3 shows the metal impurities that were removed in various rinse and filtrate solutions. The initial 0.5 mol/L *HCl* rinse was responsible for the removal of significant quantities of Pd, Sn, and Fe, and small quantities of

Pb, Ag and Cu. The gold was then leached, filtered, and precipitated. The metals remaining in the post-reduction filtrate were Pd, Sn, Fe, and Zn. Finally, the precipitated gold was rinsed using a solution of *thiourea* and *HCl* and this solution showed removal of more Pd and Ag.

- 5 [00270] **Table 3:** Summary of the impurities removed from the Experiment 2 gold in the key steps of the refining process in milligrams per litre of solution.

Sample	IC Powder Conc. Refining - Metals in Solution (mg/L)									
	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
HCl Rinse	0.6	19.9	7.4	1.4	2.7	1.7	28.9	0.7	0.5	0.1
Post-Reduction Filtrate	0.6	14.3	154.9	0.0	0.0	1.2	32.6	19.5	0.1	0.5
Thiourea Rinse	0.0	2.8	0.4	0.0	17.1	0.1	0.0	1.0	0.0	0.0

- 10 [00271] Table 4 below shows the summary of the metal impurities found in this feed gold before the leach and is followed by the impurities found in the refined gold. As evidenced by the values shown in the table, the rinse and leach processes were able to remove over 99% of the Pt, Sn, Pb, Ag, Cu, Zn, and Ni. The impurities that remain are Pd, Fe and Al, totalling 92 mg/kg. This corresponds to a purity of 99.990%.

- 15 [00272] **Table 4:** Summary of the metal impurities found in gold solid before and after the refining process in milligrams per kilogram, carried out on e-waste gold obtained from Experiment 2.

Sample	Purity (%)	IC Powder Concentrate - Impurities Present in Gold Solid (mg/kg)									
		Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Initial	99.374%	9	331	2235	30	2972	38	579	30	13	21
Refined	99.990%	0	68	0	0	0	0	22	0	0	2

- 20 [00273] Also see Summary Tables 2A-H.

[00274] Jewelry Gold: Experiment 3

- 25 [00275] The results below are from an experiment in which the same process outlined in the section "Selected Example of Chemical Processing" was used on impure gold obtained from jewelry. Table 5 shows the metal impurities that were removed in the rinse and leach processes. The initial 0.5 mol/L *HCl* rinse was responsible for the removal of Ag and Cu. The gold was then leached, filtered, and precipitated. The metals remaining in the post-reduction filtrate were Pt, Pd, Sn and Cu. Finally, the precipitated gold was rinsed using a solution of *thiourea* and *HCl* and this solution showed removal of a significant amount of Ag.

[00276] **Table 5:** Summary of the impurities removed from the Experiment 3 Jewelry gold in the key steps of the refining process in milligrams per litre of solution.

Sample	Jewelry Gold Refining - Metals in Solution (mg/L)				
	Pt	Pd	Sn	Ag	Cu
HCl Rinse	0.0	0.0	0.3	5.1	12.9
Post-Reduction Filtrate	0.1	0.2	0.2	0.0	0.7
Thiourea Rinse	0.2	0.3	0.0	34.2	0.2

5

[00277] Finally, Table 6 below shows the summary of the metal impurities found in this feed gold before the leach and is followed by the metal impurities found in the refined gold. As evidenced by the values shown in the table, the rinse and leach processes were able to remove 100% of the Pd, Sn, and Ag. The metal impurities that remain are Pt and Cu, totalling 30 mg/kg. This corresponds to a purity of 99.997%.

10

[00278] **Table 6:** Summary of the metal impurities found in gold solid before and after the refining process in milligrams per kilogram, carried out on Experiment 3 gold obtained from Jewelry.

Sample	Purity (%)	Jewelry Gold - Impurities Present in Gold (mg/kg)				
		Pt	Pd	Sn	Ag	Cu
Initial	99.886%	24	6	14	1085	13
Refined	99.997%	25	0	0	0	5

15

[00279] This work shows that gold collected from substances comprising precious metals may be refined to 9999 purity using the herein described refining method. The outlined method is shown to remove the many metallic impurities of concern that may be present in gold, including Pt, Pd, Sn, Pb, Ag, Cu, Fe, Zn, Co, Ni, and Al.

20

[00280] Also see Summary Tables 3A-H.

25

[00281] Summary Tables

[00282] Experiment 1 – E-Waste Summary Tables 1A-H

A

		Surface E-Waste - Impurities Present in Gold Solid (mg/kg)									
Sample	Purity (%)	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Co	Al
Initial	99.598%	15	17	457	1371	985	170	268	369	10	349
Refined	99.997%	0	0	0	0	21	0	0	0	0	12

5 B

	Surface E-Waste Refining - Metals in Solution (mg/L)									
Sample	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Co	Al
HCl Rinse	0.3	0.1	24.7	204.2	0.9	4.0	28.1	1.7	0.2	29.0
Post-Reduction Filtrate	0.3	0.4	11.5	0.5	7.1	8.5	4.9	6.4	0.7	7.9
Thiourea Rinse	0.0	0.1	0.0	0.2	23.4	0.3	0.0	3.5	0.0	0.1

C

E-Waste Gold Head Sample		Concentration in Solid (mg/kg)													
Sample Identification	Purity (%)	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
Head Sample	99.60%	822456	15	17	457	1371	985	170	268	369	0	10	3	1	349

D

Initial Gold Rinse	Sample Concentration (mg/L, ICP-OES)												
Sample Identification	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
0.5 M HCl Rinse	0	0	25	204	1	4	28	2	0	0	0	0	29
Water Rinse	0	0	2	41	2	1	7	2	0	0	0	0	8
Acetic Acid Rinse	0	0	1	16	0	0	3	1	0	0	0	0	3

10

E

Leach	Sample Concentration (mg/L, ICP-OES)													
Sample Identification	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
Filtrate	131414	0	1	21	12	36	16	10	62	1	1	0	0	21

F

Sodium meta-Bisulfite Reduction	Sample Concentration (mg/L, ICP-OES)													
Sample Identification	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
60 min	10.0	0.0	0.4	12.4	0.0	0.1	5.8	5.1	4.7	0.3	0.8	0.0	2.0	8.1
Filtrate	2.1	0.3	0.4	11.5	0.5	7.1	8.5	4.9	6.4	0.3	0.7	0.0	0.0	7.9
Water Rinse	5.0	0.0	0.0	0.2	3.2	1.7	0.5	0.0	1.2	0.0	0.0	0.0	0.0	0.2

G

1M Thiourea Rinse	Sample Concentration (mg/L, ICP-OES)												
Sample Identification	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
10 min	0.0	0.1	0.0	0.2	23.4	0.3	0.0	3.5	0.0	0.0	0.0	0.0	0.1
Water Rinse 1	0.0	0.1	0.7	0.0	2.5	0.3	0.0	0.6	0.0	0.0	0.0	0.0	0.0
Water Rinse 2	0.1	0.0	0.4	0.0	0.1	0.2	0.0	2.8	0.0	0.0	0.0	0.0	0.1

H

Gold Purity		Concentration in Solid (mg/kg)												
Sample Identification	Purity (%)	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
Blank	-													
Gold, Solid	99.9782%	0	10	9	0	132	3	0	30	0	0	0	0	34
Gold, Solid (Corrected)	99.9967%	0	0	0	0	21	0	0	0	0	0	0	0	12
Reverse aqua regia blank subtracted from ICP-OES results (mg/L)														

5

[00283] Experiment 2 – E-Waste Summary Tables 2A-H

A

		IC Powder Concentrate - Impurities Present in Gold Solid (mg/kg)									
Sample	Purity (%)	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Initial	99.374%	9	331	2235	30	2972	38	579	30	13	21
Refined	99.990%	0	68	0	0	0	0	22	0	0	2

B

	IC Powder Conc. Refining - Metals in Solution (mg/L)									
Sample	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
HCl Rinse	0.6	19.9	7.4	1.4	2.7	1.7	28.9	0.7	0.5	0.1
Post-Reduction Filtrate	0.6	14.3	154.9	0.0	0.0	1.2	32.6	19.5	0.1	0.5
Thiourea Rinse	0.0	2.8	0.4	0.0	17.1	0.1	0.0	1.0	0.0	0.0

10

C

E-Waste Gold Head Sample		Concentration in Solid (mg/kg)													
Sample ID	Purity (%)	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
Head Sample	99.37%	838179	9	331	2235	30	2972	38	579	30	13	0	1	1	21

D

Initial Gold Rinse	Sample Concentration (mg/L, ICP-OES)												
Sample Identification	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
0.5 M HCl Rinse	1	20	7	1	3	2	29	1	0	0	0	0	0
Water Rinse	0	3	2	1	1	1	5	2	0	0	0	0	0
Acetic Acid Rinse	0	1	7	0	14	0	3	3	0	0	0	0	0

E

Leach	Sample Concentration (mg/L, ICP-OES)													
Sample Identification	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
Filtrate	133976	1	42	276	0	32	2	62	24	0	0	0	0	0

5 F

Sodium meta-Bisulfite Reduction	Sample Concentration (mg/L, ICP-OES)													
Sample Identification	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
20 min	6	1	14	163	0	0	2	35	21	0	0	0	0	3
Filtrate	8	1	14	155	0	0	1	33	19	0	0	0	0	1
Water Rinse	4	0	1	9	0	2	0	2	1	0	0	0	0	0

G

1M Thiourea Rinse	Sample Concentration (mg/L, ICP-OES)												
Sample Identification	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
10 min	0	4	3	0	27	1	0	13	0	0	0	0	17
Filtrate	0	3	0	0	17	0	0	1	0	0	0	0	0
Water Rinse 1	0	1	0	0	0	0	0	1	0	0	0	0	0
Water Rinse 2	0	0	1	0	0	0	0	1	0	0	0	0	0

H

Gold Purity		Concentration in Solid (mg/kg)													
Sample ID	Purity (%)	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
Blank	-														
Gold, Solid	99.98%	898668	0	79	1	1	22	5	25	5	0	0	0	5	22
Gold, Solid (Corrected)	99.99%	897858	0	68	0	0	0	0	22	0	0	0	0	5	2
Reverse aqua regia blank subtracted from ICP-OES results (mg/L)															

[00284] Experiment 3 – Jewelry Summary Tables 3A-H

A

		Jewelry Gold - Impurities Present in Gold (mg/kg)				
Sample	Purity (%)	Pt	Pd	Sn	Ag	Cu
Initial	99.886%	24	6	14	1085	13
Refined	99.997%	25	0	0	0	5

B

		Jewelry Gold Refining - Metals in Solution (mg/L)				
Sample		Pt	Pd	Sn	Ag	Cu
HCl Rinse		0.0	0.0	0.3	5.1	12.9
Post-Reduction Filtrate		0.1	0.2	0.2	0.0	0.7
Thiourea Rinse		0.2	0.3	0.0	34.2	0.2

5

C

Jewelry Gold Head Sample		Concentration in Solid (mg/kg)													
Sample Identification	Purity (%)	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
Jewelry Head Sample	99.89%	884174	24	6	14	0	1085	13	0	0	0	0	0	0	0

D

Initial Gold Rinse	Sample Concentration (mg/L, ICP-OES)													
Sample Identification	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al	
0.5 M <i>HCl</i> Rinse	1	0	0	0	3	5	13	0	7	0	0	0	0	
<i>Water</i> Rinse	1	0	0	1	1	0	2	0	15	0	0	0	0	
<i>Acetic Acid</i> Rinse	0	1	0	1	0	1	1	0	5	0	0	0	0	

10

E

Leach		Sample Concentration (mg/L, ICP-OES)													
Sample Identification		Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
Filtrate		144299	6	1	1	1	67	3	0	35	0	0	0	0	4

F

Sodium meta-Bisulfite Reduction	Sample Concentration (mg/L, ICP-OES)												
Sample Identification	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
20 min	0	0	6	0	0	1	0	35	0	0	0	0	2
Filtrate	0	0	0	0	0	1	0	5	0	0	0	0	0
Water Rinse	0	0	0	0	12	1	0	1	0	0	0	0	0

G

1M Thiourea Rinse	Sample Concentration (mg/L, ICP-OES)													
Sample Identification	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
Initial														
10 min	46.5	0.2	0.3	0.0	0.0	34.2	0.2	0.0	4.4	0.0	0.0	0.0	0.0	0.5
Water Rinse 1	35	0	0	0	0	0	0	0	1	0	0	0	0	0
Water Rinse 2	143	0	0	0	0	1	0	0	1	0	0	0	0	0

H

Gold Purity														
Sample Identification	Purity (%)	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Co	Cr	Mn	Al
Blank	-													
Gold, Solid	99.930%	25	3	17	1	92	15	1	108	3	0	0	1	430
Gold, Solid (Corrected)	99.997%	25	0	0	0	0	5	0	0	2	0	0	0	0
Reverse aqua regia blank subtracted from ICP-OES results (mg/L)														

- 5 [00285] **Example 2 - Refining Precious Metals From E-Waste & Jewelry**
- [00286] **MATERIALS**
- [00287] Chemicals
- [00288] All chemicals were purchased as reagent grade and used without further purification. Acids, solvents, salts, reducing agents, and oxidants, including ultra-pure 37%
- 10 HCl, ultra-pure 70% nitric acid, ammonium chloride, magnesium chloride, ascorbic acid, iron (III) chloride, thiourea, sodium metabisulfite, sodium hydroxide, and sodium chlorate were purchased from VWR and used as received. Glacial acetic acid was purchased in bulk from Univar.
- [00289] Equipment
- 15 [00290] All glassware, weigh boats, scoopulas, pipettes, and micropipette tips were taken from new stock, and were both cleaned and stored separately from the rest of the laboratory equipment. Other necessary equipment used included magnetic stir plates, Büchner funnels and flasks, and appropriate filter papers. Analysis was carried out using Thermo Scientific iCAP PRO XP Duo instrument, using ICP grade standards from Fisher Scientific.
- 20 [00291] **ANALYSIS**
- [00292] ICP-OES
- [00293] Analysis was carried out in-house using a Thermo Scientific iCAP PRO XP Duo (ICP-OES) instrument. Standards and samples are diluted in approx. 3% HNO₃ solution using

reverse-osmosis water to match the matrix of each sample being analyzed to the standards. Argon was used as both the cooling gas and carrier gas for this instrument. Quality control samples were analyzed approximately every 10-20 samples to observe possible instrument drift and to ensure proper calibration.

5 [00294] **FEEDSTOCK**

[00295] Precious metals subjected to the herein described refining method may be extracted from any substance comprising precious metal, using any method suitable for doing so. In the present example, gold powder used in this process was obtained from two sources: e-waste and jewelry. In the case of e-waste, gold was leached using two methods: for
10 Experiment 1, a leaching process involving a pilot-scale reactor was used, with the substance comprising precious metal sourced from a combination of RAM fingers and centre-punched black CPUs; and for Experiment 2, impure gold collected from jewelry was used.

[00296] The pilot-scale reactor was a 100L reactor, the input for which was a surface gold feed (RAM fingers, centre-punched black CPU's, etc.). Said surface gold feed was
15 tumbled in the herein described refining solution to leach the surface gold. An oxidative rinse was applied to facilitate leaching efficiency. The leached solution and oxidative rinse would be gathered in a precipitation tank, degassed, and the gold would be reduced. The precipitated gold was filtered and rinsed (displacement rinse on filter) to removal of spent leach solution. The gold was then dried in an oven.

20 [00297] **CHEMICAL PROCESSING**

[00298] General Chemical Processing Procedure

[00299] Gold powder obtained from various sources was leached using a lixiviant solution, containing appropriate amounts of solvent, acid, oxidant, and ligand source, wherein the ligand may be sourced from the acid, stirring at 700 rpm at standard ambient temperature
25 and pressure conditions for twenty minutes. The lixiviant solution (otherwise referred to herein as the refining solution, or leaching mixture) was recharged regularly as needed, by adding in any one or more of the acid, oxidant, or ligand source. After completion of the leach, the solution was filtered to separate the solid by-product (for example, salts and/or other contaminants such as plastic or filter paper) and the filtrate was analyzed by ICP-OES. Based
30 on the gold content, a solution containing the appropriate amount of reducing agent was added to the filtrate and the reaction proceeded until the filtrate no longer contained gold, as analyzed by ICP-OES. The solution was then filtered to collect the gold, and then the solid powder was rinsed with a selection of solutions, as described below, before drying. After drying, 0.1 g of

the solid was treated with 20 mL of reverse aqua regia (three volumetric parts of conc. HNO_3 and one volumetric part of conc. HCl) for 20 minutes to complete dissolution of the solid. This solution was then diluted and analyzed by ICP-OES to determine purity

[00300] Selected Example of Chemical Processing

5 **[00301]** The processing began with a leaching step. A leach solution was prepared in a new 40 mL vial by mixing 5.5 g powdered gold, 16.5 mL *glacial acetic acid* as a water-miscible solvent, and 11.0 mL concentrated *HCl* as acid. After allowing the solution to homogenize, an initial volume of 0.92 mL NaClO_3 solution (40% w/w) as oxidant was added to the solution. The leach solution was dosed with another 0.92 mL *NaClO₃ solution* at 1 and 2 minutes before
10 allowing the reaction to proceed for 10 minutes to leach all the gold.

[00302] Once leaching was deemed complete (e.g., when a plateau is observed in ICP data and/or an expected gold output is reached relative to gold in the feedstock), the so formed leached solution was centrifuged, decanted, and the filtrate was collected in a new 40 mL vial with a stir bar. An aliquot was removed for analysis by ICP-OES. 15.0 mL of this leach solution
15 was added to a new 40 mL vial with a stir bar. To this vial, a solution of 0.51 g *thiourea* as reducing agent in 3.6 mL *water* was added. Once the entire volume of this solution was added, the reaction was allowed to proceed for 10 minutes.

[00303] After 10 minutes, 0.72 g *NaOH* in 3.6 mL *water* was added to the vial, and the reaction was allowed to proceed for an additional 10 minutes. After a total elapsed time of 20
20 minutes, another 0.72 g *NaOH* in 3.6 mL *water* was added to the vial, and the reaction proceeded for an additional 20 minutes. After this elapsed time of 40 minutes, an aliquot was removed and centrifuged such that the filtrate could be sampled for analysis by ICP-OES. At this point the filtrate read <5000 mg/L gold in solution, indicating that ~97% of the gold was obtained via the reduction. Said reduced gold was then centrifuged and decanted. The still
25 pregnant solution having <5000 mg/L gold in solution was set aside for later precipitation, and any resulting gold was optionally recirculated into the herein described refining method.

[00304] After the centrifugation and decanting of the gold solution, the gold solid was washed with 25 mL of *water*. Once centrifuged and decanted, the gold was washed with a second measure of 25 mL of *water*. In parallel, 12.5 mL of a 0.5 M *HCl* and 1 M *thiourea*
30 solution was prepared in a 40 mL vial with a stir bar, to be used as an acidic rinse solution. The acidic rinse solution may remove metal contaminants, such as Ag, Zn, Al. Once the *thiourea* was dissolved, the *thiourea* solution was added to the gold-containing vial and the gold was washed for 10 minutes. After 10 minutes, the stirring was stopped, and the gold was

centrifuged. Once centrifuged, an aliquot was removed for analysis by ICP-OES and then the solution was decanted. The gold was then washed with 3 measures of 12.5 mL of room temperature water, which may remove remaining trace amounts of metal contaminants, such as Pd, Ag, Cu, Zn, Al. After each rinse, the solution was centrifuged, sampled for analysis by ICP-OES, and decanted.

[00305] The gold was briefly rinsed with methanol to expedite drying. This methanol was decanted and then the gold dried on a hot plate at 110°C. Upon drying, 0.1 g of the gold was removed for digestion with reverse aqua regia for 20 minutes, allowed to degas and then dilutions of 2, 10 and 1000 times were prepared for analysis by ICP-OES. The results of this analysis were used to calculate the purity of the gold using the following Equation 2:

$$Purity \% = \left(\frac{1,000,000 - SUM \left(Impurities \text{ in } \frac{mg}{kg} \right)}{1,000,000} \right) * 100\% \quad (2)$$

[00306] RESULTS & DISCUSSION

[00307] Analysis of initial samples was carried out in-house, while analysis of final gold samples was carried out both in-house and separately by an external Third Party. To this end, the values determined in-house for the initial samples should only be generally compared, not directly compared to the values determined for the final analysis by the Third Party.

[00308] E-waste Gold: Experiment 1

[00309] The results of the ICP-OES analysis were used to track the removal of metal impurities from the gold solid or gold-containing lixiviant solution. The results in this first section are those that apply directly to the experiment described in the selected example of chemical processing above. Table 7 shows the metal impurities present in the leach, and those that remained in various rinse or filtrate solutions, meaning that these processes removed these metals. The values listed in the table below are in solution, and so are listed in mg/L - as compared to the impurities present in the solid gold in Table 8 which are listed in mg/kg. Thus, the values in Tables 7 and 8 may not be directly compared. The metal impurities in the initial leach step are shown here to show the gold selectivity of *thiourea* as a reducing agent in this procedure. Most of the metal impurities present in the leach solution, remain in the post reduction filtrate, and the fact that the numbers are lower are considered to be attributed to dilution, as the volume of the solution increases by two thirds. The metals remaining in the post-reduction filtrate are considered removed impurities. The *thiourea* rinse that the gold

underwent after precipitation removed trace amounts of Pd, Pb, Ag, Cu, Zn and Al. Finally, the water rinse that followed removed remaining trace amounts of Pd, Ag, Cu, Zn and Al.

[00310] Table 7: Summary of impurities removed from e-waste gold via key steps of the refining process in milligrams per litre of solution.

Sample	E-waste Gold Refining - Metals in Solution (mg/L)									
	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Leach	0.4	2.2	58.1	237.3	27.6	17.8	45.6	11.6	1.9	39.3
Post Reduction Filtrate	0.3	1.6	40.9	125.6	21.0	10.2	26.3	24.5	1.3	22.3
Thiourea Rinse	0.0	0.2	0.0	0.1	2.8	0.1	0.0	1.3	0.0	0.3
Water Rinse	0.0	0.1	0.0	0.0	0.2	0.1	0.0	0.9	0.0	0.3

[00311] Taking into consideration the metal impurities that have been removed, Table 8 below shows the summary of the metal impurities found in the Experiment 2 feed gold before the leach, and is followed by the metal impurities found in the refined gold, as analyzed in-house and by a 3rd Party. As evidenced by the values shown below, the leach and rinse processes were able to remove Pt, Pd, Sn, Ag, Cu, Zn, Ni, and Al. The remaining impurities were Pb and Fe, totaling 30.3 mg/kg, which corresponded to a purity of 99.997%. This same sample analyzed by the Third Party showed that the leach and rinse processes were able to remove 100% of the Pt, Pd, Sn, Pb, Cu, Zn, Ni, and Al. The metal impurities that remained were minimal amounts of Ag and Fe, totaling 46.6 mg/kg. This corresponded to a purity of 99.995%.

[00312] Table 8: Summary of impurities found in gold solid before and after the refining process in milligrams per kilogram, carried out on e-waste gold.

E-waste Gold Refining - Impurities Present in Gold (mg/kg)											
Sample	Purity (%)	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Initial	99.598%	15	17	457	1370	985	169	267	369	10	348
Refined (In-House Analysis)	99.997%	0.0	0.0	0.0	1.3	0.0	0.0	29.0	0.0	0.0	0.0
Refined (Third Party Analysis)	99.995%	0.0	0.0	0.0	0.0	14.5	0.0	32.1	0.0	0.0	0.0

[00313] Jewelry Gold: Experiment 2

[00314] The results below are from an experiment in which the same process outlined in the section “Selected Example of Chemical Processing” was used on impure gold obtained from jewelry. Table 9 shows the metal impurities present in the leach, and those that remained in various rinse or filtrate solutions, meaning that these processes removed these metals. The values listed in the table below are in solution, and as such are in mg/L - as compared to the metal impurities present in the solid gold in Table 8, which are listed in mg/kg. Thus, the values in Tables 9 and 10 may not be directly compared.

[00315] The metal impurities in the initial leach were included in Table 9 to demonstrate the gold selectivity of thiourea as a reducing agent. The gold was then leached, filtered, and precipitated; and so the metals remaining in the post-reduction filtrate were considered removed impurities. Most of the metals present in the leach solution remain in the post reduction filtrate, and the fact that the numbers were lower was considered to be attributed to dilution, as the volume of the solution increased by two thirds.

[00316] The metal impurities remaining in the post-reduction filtrate were considered removed impurities. The thiourea rinse that the gold underwent after precipitation removed trace amounts of Sn, Ag and Cu. Finally, the water rinse that followed removed remaining trace amounts of Sn, Ag and Cu.

[00317] Table 9: Summary of impurities removed from jewelry gold via steps of the refining process in milligrams per liter of solution.

Sample	E-waste Gold Refining - Metals in Solution (mg/L)					
	Pt	Pd	Sn	Ag	Cu	Fe
Leach	1.5	0.0	0.7	15.3	3.5	0.0
Post Reduction Filtrate	1.0	0.1	0.3	5.9	2.1	0.0
Thiourea Rinse	0.0	0.0	0.1	8.6	0.1	0.0
Water Rinse	0.0	0.0	0.1	0.1	0.4	0.0

[00318] Table 10 below shows the summary of the metal impurities found in this feed gold before the leach, and is followed by the metal impurities found in the refined gold, as analyzed in-house and by a Third Party. As evidenced by the values shown in the table, according to the in-house analysis, the rinse and leach processes were able to remove 100% of the Pt, Pd, Sn, Ag, Cu and Fe. This corresponded to a purity of 100.0%. This same sample analyzed by the Third Party showed that the rinse and leach processes were able to remove

100% of the Pt, Pd, Sn, and Cu. The impurities that remained were Ag and Fe totaling 50.4 mg/kg. This corresponded to a purity of 99.995%.

[00319] Table 10: Summary of metal impurities found in gold solid before and after the refining process in milligrams per kilogram, carried out on jewelry gold.

E-waste Gold Refining - Impurities Present in Gold (mg/kg)							
Sample	Purity (%)	Pt	Pd	Sn	Ag	Cu	Fe
Initial	99.969%	6.0	0.0	5.8	162.4	22.5	5.6
Refined (In-house Analysis)	100.00%	0.0	0.0	0.0	0.0	0.0	0.0
Refined (Third Party Analysis)	99.995%	0.0	0.0	0.0	19.5	0.0	30.9

[00320] This work shows that gold collected from from substances comprising precious metals may be refined to 9999 purity using the the herein described refining method. The outlined method is shown to remove the many metallic impurities of concern that may be present in gold, including Pt, Pd, Sn, Pb, Ag, Cu, Fe, Zn, Ni, and Al.

[00321] Example 3 - Refining Precious Metals from Jewelry

[00322] Generally, precious metals, such as gold, has been recovered from jewelry using either a pyrometallurgical process or aqua regia, a hydrometallurgical process. Both of these methods are costly and, to both workers and the environment, hazardous endeavors.

[00323] MATERIALS

[00324] Chemicals

[00325] All chemicals were purchased as reagent grade and used without further purification. Acids, solvents, salts, reducing agents, and oxidants including ultra-pure 37% HCl, ultra-pure 70% nitric acid, ammonium chloride, magnesium chloride, ascorbic acid, iron (III) chloride, thiourea, sodium metabisulfite, and sodium chlorate were purchased from VWR and used as received. Glacial acetic acid was purchased in bulk from Univar.

[00326] Equipment

[00327] All glassware, weigh boats, scoopulas, pipettes, and micropipette tips were taken from new stock and were both cleaned and stored separately from the rest of the laboratory equipment. Other necessary equipment used included magnetic stir plates, Büchner funnels and flasks, and appropriate filter papers. Analysis was carried out using Thermo Scientific iCAP PRO XP Duo instrument, using ICP grade standards from Fisher Scientific.

[00328] ANALYSIS**[00329] ICP-OES**

5 [00330] Analysis was carried out in-house using the Thermo Scientific iCAP PRO XP Duo (ICP-OES) instrument. Standards and samples are diluted in approx. 3% HNO₃ solution using reverse-osmosis water to match the matrix of each sample being analyzed to the standards. Argon is used as both the cooling gas and carrier gas for this instrument. Quality control samples are analyzed approximately every 10-20 samples to observe possible instrument drift and to ensure proper calibration.

[00331] FEEDSTOCK

10 [00332] Precious metals subjected to the herein described refining method may be extracted from any substance comprising precious metal, using any method suitable for doing so. In the present example, 10K jewelry gold powder used in this process was obtained by atomizing 10K jewelry to <200 µm.

15 [00333] The jewelry was atomized by first melting the jewelry to a liquid state. It was then streamed into a tank where high pressure streams of fluid impacted the molten metal stream forming particles. The size and shape of said particle may be influenced by the flow rate of the pressurized fluid, the state of the fluid, and shape of the stream. The fluid may be a gas or liquid and is typically water when liquid.

[00334] CHEMICAL PROCESSING

20 [00335] General Chemical Processing Procedure

[00336] Atomized 10K gold powder or similar was leached using a lixiviant solution (otherwise referred to herein as a refining solution or leaching mixture) containing appropriate amounts of solvent, oxidant, acid, and ligand source, stirring at 700 rpm at standard ambient temperature and pressure conditions for twenty minutes. The lixiviant solution was recharged
25 regularly as needed, by adding in any one or more of the acid, oxidant, or ligand source. After completion of the leach, the solution was filtered to separate a solid silver chloride by-product that formed and the filtrate was analyzed by ICP-OES. Based on Pd and/or Pt content, a solution containing an appropriate amount of reducing agent was added to the filtrate, and the reaction proceeded for twenty minutes until the filtrate no longer contained Pd and/or Pt, as
30 analyzed by ICP-OES. The solution was then filtered to collect the Pd and/or Pt precipitate. After completion of the Pd and/or Pt reduction, a second solution containing an appropriate amount of reducing agent was added to the filtrate and the reaction proceeded for twenty minutes until the filtrate no longer contained gold, as determined by ICP-OES. The solution

was then filtered to collect the gold as a solid powder, which was rinsed with a selection of solutions, as described below, before drying. After drying, 0.1 g of the gold powder was treated with 20 mL of reverse aqua regia (three volumetric parts of conc. HNO_3 and one volumetric part of conc. HCl) for 20 minutes to complete dissolution of the gold powder. This solution was then diluted and analyzed by ICP-OES to determine purity.

[00337] Selected Example of Chemical Processing

[00338] The processing began with a leaching step. A leach solution was prepared in a clean 600 mL beaker by mixing 180 mL *glacial acetic acid* as a water-miscible solvent, and 108 mL concentrated *HCl* as acid. 30 g of atomized 10K gold from jewelry was added to this beaker, followed by an initial volume of 5.88 mL of aqueous NaClO_3 solution (40% w/v) as oxidant. This mixture was stirred at 700 rpm on a stirring plate for the duration of the reaction. The leach solution was dosed with another 2.94 mL of NaClO_3 solution at 1, 2, 3, and 4 minutes, with an additional 2.94 mL dose, accompanied by 12 mL of concentrated *HCl* at 5 minutes as a means of recharging the lixiviant. After these doses and recharges, the reaction was allowed to proceed for 10 minutes to leach all the gold.

[00339] Once the leach was deemed completed (e.g., when a plateau is observed in ICP data and/or an expected gold output is reached relative to gold in the feedstock), the so formed leach solution was filtered to remove silver chloride precipitate, formed as a by-product; and the filtrate was collected in a new 600 mL beaker with a stir bar. An aliquot was removed for analysis by ICP-OES.

[00340] To the filtrate, 4.41 mL of NaClO_3 solution was added, followed immediately by a saturated *ammonium chloride* solution, 1.909 g of *ammonium chloride* in 5.10 mL of *water*. The mass of ammonium chloride added was based on mass of Pt and Pd in solution, as identified by ICP-OES, multiplied by 30. This solution was stirred for 20 minutes to reduce Pt and/or Pd in solution. Once this reduction was complete, the solution was filtered to collect the precipitated Pt and/or Pd, and the filtrate was transferred to a new 600 mL beaker, and an aliquot was removed for analysis by ICP-OES. This solution was degassed for 20 minutes by stirring at 1000 rpm.

[00341] After degassing, a saturated solution of *thiourea*, 2.7 g in 19.0 mL of *water* was added as reducing agent to the degassed solution, and allowed to stir for 10 minutes. After 10 minutes, 65.2 mL of a 5 M *sodium hydroxide* solution was added and the solution allowed to stir for an additional 10 minutes to precipitate any remaining gold in solution. The solution was then filtered by vacuum to collect the gold, and the solid gold was rinsed with 60 mL *water*.

This rinse serves to both rinse the gold of contaminants as well as spent lixiviant, thiourea solution, etc.

[00342] The so-collected gold was briefly rinsed with methanol to expedite drying. This methanol was decanted and then the gold dried on a hot plate at 110°C. Upon drying, 0.1 g of the gold was removed for digestion with reverse aqua regia for 20 minutes, allowed to degas and then dilutions of 2, 10 and 1000 times were prepared for analysis by ICP-OES. The results of this analysis were used to calculate the purity of the gold using the following Equation 3:

$$Purity \% = \left(\frac{1,000,000 - SUM \left(Impurities \text{ in } \frac{mg}{kg} \right)}{1,000,000} \right) * 100\% \quad (3)$$

[00343] RESULTS & DISCUSSION

[00344] Table 11 below contains the approximate make-up of the 10K atomized jewelry gold that was used, as described in “Selected Example of Chemical Processing”. The composition is provided in mg/kg and was obtained by digesting 0.1 g of jewelry in a solution of reverse aqua regia, 3:1 HNO₃:HCl. This solution was then analysed by ICP-OES. This analysis gave an estimate of the amount of gold that could be expected from processing said feedstock.

[00345] Table 11: Summary of metal composition of 10K atomized jewelry gold, as digested by reverse aqua regia, in mg/kg.

	Concentration of metals in solid (mg/kg)									
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni
10K Jewelry	464151	1513	805	1689	269	121000	277289	1565	36316	4707

[00346] Table 12 below shows the metals in solution upon completion of the jewelry leach. These values are provided in mg/L, as they are in solution, and therefore they cannot be directly compared to those provided in Table 11 - but may be compared proportionally. It was found that a significant portion of the silver in the starting material was converted into insoluble silver chloride salt, which is why the value of the remaining soluble silver leached into solution is very low compared to the initial feed.

[00347] Table 12: Summary of metal composition of the leach filtrate from leaching 10K jewelry, provided in mg/L.

Leach Filtrate Analysis	Concentration of metals in jewelry leach filtrate (mg/L)									
Sample Identification	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni
Jewelry Leach	36769	118	80	179	24	159	31949	146	3502	491

[00348] Following the jewelry leach and the first filtration, the precipitation of Pt and/or Pd was carried out using *ammonium chloride*. The results of this precipitation are shown in Table 13, where it is shown that the Pt and Pd in solution was removed. Any other discrepancies to numbers compared to those shown in Table 2 are attributed to the dilution of the solution following the addition of the saturated *ammonium chloride* solution.

10 [00349] Table 13: Summary of metal composition of the leach filtrate from leaching 10K jewelry following Pd/Pt reduction and removal by ammonium chloride, provided in mg/L.

Pd/Pt Reduction	Concentration of metals in post-Pd/Pt reduction filtrate (mg/L)									
Sample Identification	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni
Post-Pd/Pt Reduction	32142	0	0	171	17	105	28737	138	3332	463

[00350] Once the Pd and Pt was precipitated out of the solution, the remaining leach filtrate was treated with a saturated *thiourea* solution to precipitate out the gold in solution. The data in Table 14 shows the impurities left in solution following this precipitation procedure. The gold was recovered without significantly affecting the other impurities in solution. Any discrepancies of the values between those in Table 3 and Table 4 may be attributed to the dilution of the filtrate that occurs upon the addition of the saturated *thiourea* solution, and 5M *sodium hydroxide* solution.

20 [00351] Table 14: Summary of metal impurities remaining in solution after reduction of gold, provided in mg/L.

Gold Reduction	Concentration of metals in post-Au reduction filtrate (mg/L)									
Sample Identification	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni
Reduction Residue	11	0	0	113	13	78	23867	114	2765	382

[00352] Finally, reverse aqua regia was carried out on a small sample of the gold powder solid to determine the purity. Table 15 below shows the summary of the impurities

found in this gold powder solid following the leach of 10K jewelry gold. As evidenced by the values shown in the table, the leach and precipitation processes were selective for gold, and the outlined chemical process may achieve a gold purity of 99.97%.

[00353] Table 15: Summary of metal impurities found in gold following the leach and precipitation of 10K Jewelry by the method as described herein, given in mg/kg.

Gold Purity		Concentration of metal impurities in solid gold (mg/kg)									
Sample Identification	Purity (%)	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	
Reduction Output	99.97%	6.0	0.0	5.8	1.8	162	22.5	5.6	85.7	0.8	

[00354] The experiment described in “Selected Example of Chemical Processing”, was carried out using *thiourea* as the reducing agent for gold. However, other reducing agents may be used in place of thiourea, with minimal changes to the procedure. If using other reducing agents, the procedure is the same for the leaching step and Pd and/or Pt reduction; but once the gold reduction step is reached, *sodium hydroxide* addition is not necessary. Sodium hydroxide tends to be added to increase reaction kinetics, but tends not to be needed for non-thiourea reductants - and may be optional even with thiourea reductants.

[00355] The results that follow are those from an experiment where *sodium metabisulfite* was used as reducing agent. It was added in an amount 2 times the mass of gold in solution, as a saturated or 3.4M solution. As starting leach solutions are different, the values cannot be directly compared, but the values outlined in Table 12 are representative of the metals in the jewelry leach filtrate, as the feedstock was the same, as well as the phase ratio of the reaction.

[00356] As evidenced by the values listed in Table 16 below, the reduction was effective, but not as selective as the reduction using *thiourea*, as it precipitated more Ag and Pb than thiourea. Some metals were precipitated entirely or almost entirely by *sodium metabisulfite* and not *thiourea*, such as lead and silver.

[00357] Table 16: Summary of metal impurities remaining in leach filtrate following precipitation of gold using sodium metabisulfite or thiourea as reducing agents, given in mg/L.

Gold Reduction	Concentration of metals in post-gold reduction filtrate (mg/L)									
Reducing Agent	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni
Sodium meta-Bisulfite	3.3	0	1.3	110	0	3.4	24116	126	2872	383
Thiourea	11.4	0	0	113	13.3	78.2	23867	114	2765	382

[00358] The herein described refining process was carried out on 10K jewelry, which is among the lowest purity jewelry gold that is produced - and as such, it expected to work similarly on jewelry gold of higher purities and also on Doré bars.

5 [00359] **Example 4 - Refining Precious Metals with Heated and Non-heated Rinses**

[00360] **MATERIALS**

[00361] Chemicals

[00362] All chemicals in this study were purchased as reagent grade and used without further purification. Acids, solvents, salts, reducing agents, and oxidants including ultra-pure
10 37% HCl, ultra-pure 70% nitric acid, ammonium chloride, magnesium chloride, ascorbic acid, iron (III) chloride, thiourea, sodium metabisulfite, and sodium chlorate were purchased from VWR and used as received. Glacial acetic acid was purchased in bulk from Univar.

[00363] Equipment

[00364] For this study, all glassware, weigh boats, scoopulas, pipettes, and micropipette
15 tips were taken from new stock and were both cleaned and stored separately from the rest of the laboratory equipment. Other necessary equipment used included magnetic stir plates, Büchner funnels and flasks, and appropriate filter papers. Analysis was carried out using Thermo Scientific iCAP PRO XP Duo instrument, using ICP grade standards from Fisher Scientific.

20 [00365] **ANALYSIS**

[00366] ICP-OES

[00367] Analysis was carried out in-house using the Thermo Scientific iCAP PRO XP Duo (ICP-OES) instrument. Standards and samples are diluted in approx. 3% HNO₃ solution using reverse-osmosis water to match the matrix of each sample being analyzed to the
25 standards. Argon is used as both the cooling gas and carrier gas for this instrument. Quality control samples are analyzed approximately every 10-20 samples to observe possible instrument drift and to ensure proper calibration.

[00368] **FEEDSTOCK**

[00369] The gold powder for use in this process is obtained from two sources: e-waste
30 and jewelry. In the case of e-waste, gold was leached using two methods: for Experiments 1 and 2, the e-waste was sourced from a combination of RAM fingers and centre-punched black CPUs and processed to remove non-gold containing components prior to leaching and refining; and for Experiments 3 and 4, impure gold collected from jewelry was used.

[00370] CHEMICAL PROCESSING**[00371] General Chemical Processing Procedure**

[00372] Gold powder obtained from various sources was first rinsed with a selection of solutions. After rinsing, the gold powder was leached using a lixiviant solution (otherwise referred to herein as the refining solution, or leaching mixture) containing appropriate amounts of solvent, oxidant, and ligand, stirring at 700 rpm at standard ambient temperature and pressure conditions for twenty minutes. The lixiviant solution was recharged regularly as needed. After completion of the leach, the solution was filtered to separate solid byproduct and the filtrate was analyzed by ICP-OES. Based on the gold content, a solution containing the appropriate amount of reducing agent was added to the filtrate and the reaction proceeded until the filtrate no longer contained gold, as analyzed by ICP-OES. The solution was then filtered to collect the gold, and then the solid powder was rinsed with a selection of solutions before drying. After drying, 0.1 g of the solid was treated with 20 mL of reverse aqua regia (three volumetric parts of conc. HNO_3 and one volumetric part of conc. HCl) for 20 minutes to complete dissolution of the solid. This solution was then diluted and analyzed by ICP-OES to determine purity.

[00373] Selected Example of Chemical Processing

[00374] 17.5 mL of a 0.5 mol/L HCl and 1 M *thiourea* solution was prepared in a 40 mL vial fitted with an appropriately sized stir bar. Subsequently, 3.5 g of e-waste gold was added to this vial and rinsed with stirring at approx. 700 rpm in this solution for 10 minutes. After 10 minutes, the stirring was stopped, and the gold was allowed to settle. Once settled, an aliquot was removed for analysis by ICP-OES and then the solution was decanted. The gold was then washed with 17.5 mL and 7 mL of 60°C distilled *water* and *glacial acetic acid* respectively. After each rinse, the solution was centrifuged, sampled for analysis by ICP-OES, and decanted.

[00375] A leach solution was prepared in a new 40 mL vial by mixing 10.5 mL *glacial acetic acid*, 7.0 mL concentrated HCl , and 0.9 g MgCl_2 . After allowing the MgCl_2 to slightly dissolve, an initial volume of 0.6 mL NaClO_3 solution (40% w/w) was slowly added to the solution, followed immediately by all the previously rinsed gold. The leach solution was dosed with another 0.6 mL NaClO_3 solution at 3 and 6 minutes before allowing the reaction to proceed for 15 minutes to leach all the gold.

[00376] Once the leach was completed, the solution was centrifuged, decanted, and the filtrate was collected in a new 40 mL vial with a stir bar. An aliquot was removed for analysis

by ICP-OES. To this beaker, a solution of 7.0 g *sodium metabisulfite* in 10.7 mL *water* was slowly added. Once the entire volume of this solution was added, the reaction was allowed to proceed for 20 minutes. After 20 minutes, an aliquot was removed and centrifuged such that the filtrate could be sampled for analysis by ICP-OES. Once the analysis of this filtrate reads

5 <10 mg/L gold in solution, it may be filtered by vacuum. If there is still >10 mg/L gold in solution, the reaction should be allowed to proceed and sampled every 10 minutes until the filtrate reads <10 mg/L gold.

[00377] After the centrifugation and decanting of the gold solution, the gold solid was washed with 17.5 mL of *water*. Once centrifuged and decanted, the gold was washed with a

10 second measure of 17.5 mL of *water*. In parallel, 17.5 mL of a 0.5 M *HCl* and 1 M *thiourea* solution was prepared in a 50 mL beaker with a stir bar. Once the *thiourea* is dissolved, the *thiourea* solution was added to the gold-containing vial and the gold was washed for 10 minutes. After 10 minutes, the stirring was stopped, and the gold was centrifuged. Once centrifuged, an aliquot is removed for analysis by ICP-OES and then the solution is decanted.

15 The gold was then washed with 17.5 mL of 60°C *water*, followed by two measures of 17.5 mL room-temperature *water*. After each rinse, the solution was centrifuged, sampled for analysis by ICP-OES, and decanted.

[00378] The gold was briefly rinsed with methanol to expedite drying. This methanol was decanted and then the gold dried on a hot plate at 110°C. Upon drying, 0.1 g of the gold was

20 removed for digestion with reverse aqua regia for 20 minutes, allowed to degas and then dilutions of 2, 10 and 1000 times were prepared for analysis by ICP-OES. The results of this analysis were used to calculate the purity of the gold using the following Equation 1:

$$Purity \% = \left(\frac{1,000,000 - SUM \left(Impurities \text{ in } \frac{mg}{kg} \right)}{1,000,000} \right) * 100\% \quad (1)$$

[00379] RESULTS & DISCUSSION

25 [00380] The experiment described above was performed on e-waste gold, with a rinse containing *thiourea* and *HCl* solution at room-temperature - or “cold”, as it referred to in the following discussion. This rinse was carried out before and after the leach of the gold, and it was followed by a hot, 60°C *water* rinse both before and after the leach.

[00381] The other experiments discussed in the following section follow the same

30 experimental details on gold obtained from jewelry, and a similar experiment performed on

gold obtained from both e-waste and jewelry, where both the *thiourea* and *HCl* rinses and the *water* rinses are hot, or 60°C.

[00382] *A note on purity discussions carried out in the following section. The analysis of the initial samples was carried out in-house, while the analysis of the final gold samples is carried out both in-house and a Third Party. This makes it difficult to directly compare the values provided for the initial feed and the purity analysis from the Third Party, but it provides a good comparison.

[00383] E-waste Gold: Experiment 1

[00384] The results of the ICP-OES analysis were used to track the removal of contaminating metals from the gold solid or gold-containing lixiviant solution. The results in this first section are those that apply directly to the experiment described in the “Selected Example of Chemical Processing” above. Table 4A shows the impurities that remained in various rinse or filtrate solutions, meaning that these processes removed these metals. The values listed in the table below are in solution and are as such in mg/L as compared to the impurities present in the solid gold in Table 2 which are listed in mg/kg. Thus, the values in Tables 1 and 2 may not be directly compared. The initial cold *thiourea* rinse that the gold underwent prior to the leach is responsible for removing a large amount of Pb, and lower but still significant amounts of Ag, Sn, Cu, Fe and Al. The 60°C *water* rinse that follows is responsible for removing another significant amount of Pb, and some additional Ag, Fe and Al. The gold was then leached, filtered, and precipitated, and so the metals remaining in the post-reduction filtrate are considered removed impurities. These metals included Pd, Sn, Cu, Fe, Zn and Al. The cold *thiourea* and *HCl* rinse of the precipitated gold removes a significant amount of Ag that is left in the solid gold. Finally, the last 60°C *water* rinse removes trace amounts of Sn and Ag.

[00385] Table 4A: Summary of key impurities removed from e-waste gold in key steps of the above-described refining process in milligrams per litre of solution.

Sample	Temp (°C)	E-waste Gold Refining - Metals in Solution (mg/L)									
		Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Cold Thiourea Rinse (Pre-Leach)	-	0.3	0.2	35.3	247.9	54.6	5.6	36.6	1.1	0.5	36.5
Hot Water Rinse (Pre-Leach)	60.0	0.1	0.1	0.4	33.8	2.3	0.9	7.1	1.2	0.1	8.6
Post-Reduction Filtrate	-	0.0	1.0	12.3	0.0	0.9	6.8	5.8	9.3	0.6	9.7

		E-waste Gold Refining - Metals in Solution (mg/L)									
Cold Thiourea Rinse (Post-Leach)	-	0.0	0.0	1.0	0.2	44.1	0.1	0.0	0.4	0.0	0.0
Hot Water Rinse (Post-Leach)	60.0	0.0	0.0	1.0	0.0	2.1	0.1	0.0	0.9	0.0	0.0

[00386] Taking into consideration the impurities that were removed, Table 4B below shows the summary of impurities found in the pilot-scale reactor feed gold before leaching and is followed by the impurities found in the refined gold, as analyzed in-house and by a Third Party.

[00387] As evidenced by the values obtained in-house as shown below, the rinse and leach processes were able to remove 100% of the impurities listed. There were no remaining impurities that were notable to the analysis. This corresponds to a purity of 99.999%. This same sample analyzed by Third Party showed that the rinse and leach processes were able to remove 100% of the Sn, Pb, Cu, and Fe. The impurities that remained were minimal amounts of Pt, Pd, Zn, Ni and Al and an amount of Ag, totaling 126.9 mg/kg. This corresponded to a purity of 99.987%.

[00388] Table 4B: Summary of key impurities found in gold solid before and after the above-described refining process in milligrams per kilogram, carried out on e-waste gold.

		E-waste Gold Refining - Impurities Present in Gold (mg/kg)									
Sample	Purity (%)	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Initial	99.598%	15.3	17.4	457.3	1370.6	985.0	169.8	267.8	369	10	348.7
Refined (In-House Analysis)	99.999%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Refined (Third Party Analysis)	99.987%	1.1	1.2	0.0	0.0	107.9	0.0	0.0	1.7	7.0	8.0

[00389] E-waste Gold: Experiment 2

[00390] The results in this section are from an experiment in which a similar process as outlined in the section "Selected Example of Chemical Processing" was carried out, with the only difference being that all rinses were carried out at 60°C.

[00391] Table 4C shows impurities that were removed in various rinse and filtrate solutions. The initial 60°C thiourea and HCl rinse that the gold underwent prior to leaching

removed a large amount of Pb, and lower but still notable amounts of Ag, Sn, Cu, Fe and Al. The 60°C *water* rinse that followed was responsible for removing another notable amount of Pb, and some additional Ag, Fe and Al. The gold was then leached, filtered, and precipitated, and so the metals remaining in the post-reduction filtrate are considered removed impurities.

- 5 These metals included Cu, Fe, Zn and Al. The 60°C *thiourea* and *HCl* rinse of the precipitated gold removed a notable amount of Ag that is left in the solid gold. Finally, the last 60°C *water* rinse removed additional Ag.

- 10 **[00392]** Table 4C: Summary of key impurities removed from e-waste gold in key steps of the above-described refining process in milligrams per litre of solution.

Sample	Temp (°C)	E-waste Gold Refining - Metals in Solution (mg/L)									
		Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Hot Thiourea Rinse (Pre-Leach)	60.0	0.5	0.1	27.5	251.4	50.9	8.7	45.2	1.5	0.7	45.0
Hot Water Rinse (Pre-Leach)	60.0	0.0	0.0	0.1	35.2	9.4	1.3	6.2	0.9	0.1	6.1
Post-Reduction Filtrate	-	0.0	0.4	19.1	0.4	0.2	8.2	7.9	10.6	1.1	20.6
Hot Thiourea Rinse (Post-Leach)	60.0	0.0	0.1	0.4	0.1	32.7	0.2	0.0	0.7	0.0	0.1
Hot Water Rinse (Post-Leach)	60.0	0.0	0.0	0.0	0.0	16.1	0.1	0.0	1.6	0.0	0.1

- 15 **[00393]** Table 4D below shows the summary of impurities found in this feed gold before leaching and is followed by impurities found in the refined gold, as analyzed in-house and a Third Party. As evidenced by the values shown in the table, according to in-house analysis, the rinse and leach processes were able to remove 100% of the listed impurities, and there were no remaining impurities that were notable to the analysis. This corresponded to a purity of 99.999%. This same sample analyzed by Third Party showed that the rinse and leach processes were able to remove 100% of the Sn, Pb, Cu, and Fe. The impurities that remained were Pt, Pd, Ag, Zn, Ni, and Al, totaling 63.2 mg/kg. This corresponded to a purity of 99.994%.

- 20 **[00394]** Table 7D: Summary of key impurities found in gold solid before and after the above-described refining process in milligrams per kilogram, carried out on e-waste gold.

Sample	Purity (%)	E-waste Gold Refining - Impurities Present in Gold (mg/kg)									
		Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Initial	99.598%	15.3	17.4	457.3	1370.6	985.0	169.8	267.8	369	10	348.7

		E-waste Gold Refining - Impurities Present in Gold (mg/kg)									
Refined (In-house Analysis)	99.999%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Refined (Third Party Analysis)	99.994%	0.9	1.2	0.0	0.0	43.4	0.0	0.0	1.7	14.0	2.0

[00395] Jewelry Gold: Experiment 3

[00396] The results below are from an experiment in which the same process outlined in the section "Selected Example of Chemical Processing" was used on impure gold obtained from jewelry.

[00397] Table 4E shows impurities that were removed in the rinse and leach processes. The initial cold *thiourea* rinse that the gold underwent prior to the leach removed a notable amount of Ag. The 60°C *water* rinse that followed was responsible for removing additional Ag. The gold was then leached, filtered, and precipitated, and so the metals remaining in the post-reduction filtrate are considered removed impurities. These metals included trace amounts of Pt, Pd, Sn, Ag and Cu. The cold *thiourea* and *HCl* rinse of the precipitated gold removed another smaller amount of Ag that was left in the solid gold. Finally, the last 60°C *water* rinse removed Sn.

[00398] Table 4E: Summary of key impurities removed from jewelry gold in key steps of the above-described refining process in milligrams per litre of solution.

		Jewelry Gold Refining - Metals in Solution (mg/L)				
Sample	Temp (°C)	Pt	Pd	Sn	Ag	Cu
Cold Thiourea Rinse (Pre-Leach)	-	0.3	0.3	0.0	362.6	1.0
Hot Water Rinse (Pre-Leach)	60.0	0.3	0.2	0.1	8.7	0.1
Post-Reduction Filtrate	-	0.2	0.6	0.3	2.4	0.6
Cold Thiourea Rinse (Post-Leach)	-	0.4	0.2	0.5	19.6	0.2
Hot Water Rinse (Post-Leach)	60.0	0.3	0.1	1.8	0.4	0.1

[00399] Table 4F below shows the summary of impurities found in the feed gold before leaching and is followed by impurities found in the refined gold, as analyzed in-house and a Third Party. As evidenced by the values shown in the table, according to the in-house analysis, the rinse and leach processes were able to remove 100% of the Pd, Sn, Ag and Cu. The impurity that remained was Pt and totaled 0.1 mg/kg. This corresponded to a purity of 99.997%. This same sample analyzed by Third Party shows that the rinse and leach processes were

able to remove 100% of the Sn, and Cu. The impurities that remained were Pt, Pd, and Ag, totaling 42.6 mg/kg. This corresponded to a purity of 99.992%.

[00400] Table 4F: Summary of key impurities found in gold solid before and after the above-described refining process in milligrams per kilogram, carried out on jewelry gold.

Sample	Purity (%)	Jewelry Gold Refining - Impurities Present in Gold (mg/kg)				
		Pt	Pd	Sn	Ag	Cu
Initial	99.886%	24.0	6.0	14.0	1085	13.0
Refined (In-House Analysis)	99.997%	0.1	0.0	0.0	0.0	0.0
Refined (Third Party Analysis)	99.992%	1.4	1.1	0.0	40.1	0.0

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[00401] Jewelry Gold: Experiment 4

[00402] The results below are from an experiment in which the same process outlined in the section “Selected Example of Chemical Processing” was used on impure gold obtained from jewelry, with the only change to the procedure being that all rinses were carried out at 60°C. Table 4G shows impurities that were removed in the rinse and leach processes. The initial 60°C thiourea and HCl rinse that the gold underwent prior to the leach removed a large amount of Ag. The 60°C water rinse that followed was responsible for removing additional Ag. The gold was then leached, filtered, and precipitated, and so the metals remaining in the post-reduction filtrate are considered removed impurities. These metals included trace amounts of Pt, Pd, Sn, Ag and Cu. The 60°C thiourea and HCl rinse of the precipitated gold removed another smaller amount of Ag that was left in the solid gold. Finally, the last 60°C water rinse removed trace Pt and Ag.

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[00403] Table 4G: Summary of key impurities removed from jewelry gold in the key steps of the above-described refining process in milligrams per litre of solution.

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Sample	Temp (°C)	Jewelry Gold Refining - Metals in Solution (mg/L)				
		Pt	Pd	Sn	Ag	Cu
Hot Thiourea Rinse (Pre-Leach)	60.0	0.8	0.4	0.0	336.0	1.0
Hot Water Rinse (Pre-Leach)	60.0	0.2	0.1	0.0	7.5	0.2
Post-Reduction Filtrate	-	0.1	0.1	2.0	0.2	1.0
Hot Thiourea Rinse (Post-Leach)	60.0	0.8	0.2	0.0	23.1	0.3
Hot Water Rinse (Post-Leach)	60.0	0.2	0.0	0.0	0.8	0.0

[00404] Table 4H below shows the summary of impurities found in the feed gold before leaching and is followed by impurities found in the refined gold, as analyzed in-house and by a Third Party. As evidenced by the values shown in the table, according to the in-house analysis, the rinse and leach processes were able to remove 100% of the Pd, Sn, Ag and Cu.

5 The impurity that remained was Pt and totaled 0.1 mg/kg. This corresponded to a purity of 99.998%. This same sample analyzed by Third Party shows that the rinse and leach processes were able to remove 100% of the Sn, and Cu. The impurities that remained were Pt, Pd, and Ag, totaling 87.2 mg/kg. This corresponded to a purity of 99.987%.

10 [00405] Table 4H: Summary of key impurities found in gold solid before and after the above-described refining process in milligrams per kilogram, carried out on jewelry gold.

Sample	Purity (%)	Jewelry Gold Refining - Impurities Present in Gold (mg/kg)				
		Pt	Pd	Sn	Ag	Cu
Initial	99.886%	24.0	6.0	14.0	1085	13.0
Refined (In-house Analysis)	99.998%	0.1	0.0	0.0	0.0	0.0
Refined (Third Party Analysis)	99.987%	1.8	1.5	0.0	83.9	0.0

[00406] The foregoing demonstrates that refined gold collected the above-described refining method may be refined to 9999 purity. The outlined process was shown to remove

15 many metallic impurities of concern that may be present in gold. These impurities include Pt, Pd, Sn, Pb, Ag, Cu, Fe, Zn, Ni, and Al.

[00407] Example 5 - Refining Precious Metals Using Aqueous Solutions

[00408] MATERIALS

20 [00409] Chemicals

[00410] All chemicals in this study were purchased as reagent grade and used without further purification. Acids, solvents, salts, reducing agents, and oxidants including ultra-pure 37% HCl, ultra-pure 70% nitric acid, thiourea, and sodium chlorate were purchased from VWR and used as received. Glacial acetic acid was purchased in bulk from Univar.

25 [00411] Equipment

[00412] For this study, all glassware, weigh boats, scoopulas, pipettes, and micropipette tips were taken from new stock and were both cleaned and stored separately from the rest of the laboratory equipment. Other necessary equipment used included magnetic stir plates,

Büchner funnels and flasks, and appropriate filter papers. Analysis was carried out using Thermo Scientific iCAP PRO XP Duo instrument, using ICP grade standards from Fisher Scientific.

[00413] ANALYSIS

5 **[00414] ICP-OES**

[00415] Analysis was carried out in-house using the Thermo Scientific iCAP PRO XP Duo (ICP-OES) instrument. Standards and samples are diluted in approx. 3% HNO₃ solution using reverse-osmosis water to match the matrix of each sample being analyzed to the standards. Argon is used as both the cooling gas and carrier gas for this instrument. Quality control samples are analyzed approximately every 10-20 samples to observe possible instrument drift and to ensure proper calibration.

[00416] FEEDSTOCK

[00417] The gold powder for use in this process is collected from e-waste and impure gold recovered from jewelry.

15 **[00418] CHEMICAL PROCESSING**

[00419] General Chemical Processing Procedure

[00420] Gold powder obtained from various sources was leached using a lixiviant solution (otherwise referred to herein as the refining solution, or leaching mixture) containing appropriate amounts of solvent, oxidant, and ligand, stirring at 700 rpm at standard ambient temperature and pressure conditions for twenty minutes. The lixiviant solution was recharged regularly as needed. After completion of the leach, the solution was filtered to separate the solid byproduct, and the filtrate was analyzed by ICP-OES. Based on the gold content, a solution containing the appropriate amount of reducing agent was added to the filtrate and the reaction proceeded until the filtrate no longer contained gold, as analyzed by ICP-OES. The solution was then filtered to collect the gold, and then the solid powder was rinsed with a selection of solutions before drying. After drying, 0.5 g of the solid was treated with 20 mL of reverse aqua regia (three volumetric parts of conc. HNO₃ and one volumetric part of conc. HCl) for 20 minutes to complete dissolution of the solid. This solution was then diluted and analyzed by ICP-OES to determine purity.

30 **[00421] Selected Example of Chemical Processing**

[00422] A leach solution was prepared in a clean 400mL beaker with a magnetic stir bar, by mixing 48 mL *RO water* and 90 mL *glacial acetic acid*. 132 mL of concentrated *hydrochloric acid* was added to the beaker. Following this, 60 g of powdered gold was added

to this beaker. Once the solution was homogenized, an initial volume of 10 mL of aqueous NaClO_3 solution (40% w/v) was added. This mixture was stirred at 700 rpm on a stirring plate and covered to minimize degassing for the duration of the reaction. The leach solution was dosed with another 10 mL of NaClO_3 solution at 1 and 2 minutes. After these recharges, the
 5 reaction was allowed to proceed for 10 minutes to leach all the gold.

[00423] Once the leach was completed, the solution was filtered to remove sodium and silver chloride precipitate, and the filtrate was collected in a new 400 mL beaker with a stir bar. An aliquot was removed for analysis by ICP-OES. This beaker was placed into a pre-prepared hot water bath at 60°C on a stirring hot plate and allowed to agitate in this hot bath for ~5
 10 minutes to come up to temperature. Once the desired temperature was reached, a saturated solution of *thiourea*, 12 g in 84.5 mL of *water* was added to the beaker and allowed to stir at maximum agitation for 30 minutes. The solution was then filtered by vacuum to collect the gold, and the solid rinsed with 300 mL *water*.

[00424] The gold was placed on a hot plate to dry completely. Upon drying, 0.5 g of the
 15 gold was removed for digestion with reverse aqua regia for 40 minutes, allowed to degas and then dilutions of 10, 100 and 10000 times were prepared for analysis by ICP-OES. The results of this analysis were used to calculate the purity of the gold using the following Equation 1:

$$\text{Purity \%} = \left(\frac{1,000,000 - \text{SUM} \left(\text{Impurities in } \frac{\text{mg}}{\text{kg}} \right)}{1,000,000} \right) * 100\% \quad (1)$$

[00425] The dried gold was also subjected to a 200 mL *thiourea* rinse of composed of 1
 20 mol/L *thiourea*, and 0.5 mol/L *hydrochloric acid* in *water*. This rinse was carried out by stirring the gold in this aqueous rinse for 10 minutes before decanting and displacing with *water*. The gold was then dried again, and the purity of the gold determined using the above Equation 1.

[00426] RESULTS & DISCUSSION

[00427] Experiment1

25 [00428] The results below are from the experiment described above in the “Selected Example of Chemical Processing”. Table 5A shows the impurities present in the leach, and those that remained in the filtrate solution, meaning that these processes removed these metals. The values listed in the table below were in solution and are as such in mg/L - as compared to impurities present in the solid gold as shown in Table 5B, which are listed in
 30 mg/kg. Thus, the values in Tables 5A and 5B may not be directly compared. The impurities in the initial leach are shown here to show the gold selectivity of *thiourea* as a reducing agent in

this procedure. The gold was leached, filtered, and precipitated, and so the metals remaining in the post-reduction filtrate are considered removed impurities. Most of the metals present in the leach solution remained in the post reduction filtrate, and the fact that the numbers are lower may be attributed to dilution, as the volume of the solution increased. The metals remaining in the post-reduction filtrate were considered removed impurities.

[00429] Table 5A: Summary of key impurities removed from the gold in the key steps of the above-described refining process in milligrams per litre of solution.

Leach Filtrate Analysis	Concentration of metals in gold leach filtrate (mg/L)									
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni
Gold Leach	184547	1.1	4.4	3.4	0.7	37.7	194.6	8.5	75.1	3.9
Reduction Residue	76	0.9	4.1	5.2	0.8	30.1	176.1	8.3	34.9	4.2

[00430] Table 5B below shows the summary of impurities found in the feed gold before leaching and is followed by impurities found in the refined gold, as analyzed in-house and by a Third Party. As evidenced by the values shown in the table, according to the in-house analysis, the leach and reduction processes were able to remove 100% of the Pt, Pd, Pb, Zn and Ni. The Ag and Cu were removed in a large amount. This corresponded to a purity of 99.994%. This same sample analyzed by Third Party shows that the leach and reduction processes were able to remove 100% of the Pt, Pd, Pb, Cu, Zn and Ni. This resulted in a purity of 99.996%.

[00431] Table 5B: Summary of key impurities found in gold solid before and after the above-described refining process in milligrams per kilogram, carried out on powdered gold.

		Gold Refining - Impurities Present in Gold (mg/kg)									
Sample	Purity (%)	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Head Sample (In-House Analysis)	99.82%	4	29	19	4	569	864	28	175	16	20
Refined (In-house Analysis)	99.994%	0	0	5	0	18	12	6	0	0	20
Refined (Third Party Analysis)	99.997%	0	0	4	0	21	0	3	0	0	1

[00432] The leach and precipitation processes were followed by the *thiourea* rinse. In Table 5C, it is shown that the gold that underwent this rinse after precipitation and drying, this rinse was responsible for removing trace amounts of Sn, Ag, Fe, Cu and Zn.

5 [00433] Table 5C: Summary of key impurities removed by the thiourea rinse from gold in the above-described refining rinse process in milligrams per litre of solution.

Sample	Gold Refining - Metals in Solution (mg/L)									
	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Thiourea Rinse	0.0	0.0	0.2	0.0	2.9	2.0	0.2	2.3	0.1	0.2

[00434] Table 5D below shows the purities as measured in-house and by a Third Party, after the *thiourea* rinse. At this point, 100% of the Ag was removed, resulting in an improved
10 purity to 99.998%.

[00435] Table 5D: Summary of key impurities found in gold solid before and after the above-described refining process, including the thiourea rinse, in milligrams per kilogram, carried out on powdered gold.

Sample	Purity (%)	Gold Refining - Impurities Present in Gold (mg/kg)									
		Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Head Sample (In-house Analysis)	99.82%	4	29	19	4	569	864	28	175	16	20
Refined (In-house Analysis)	99.996%	0	0	5	0	4	6	7	0	0	17
Refined (Third Party Analysis)	99.998%	0	0	4	0	0	0	3	0	0	1

15 [00436] The foregoing demonstrates that refined gold collected from the above-described refining method may be refined to 9999 purity. The outlined process was carried out on gold with an initial purity of 99.82%, but is expected to work in the same manner when starting with a gold of lesser purity (for example, < 95%). This process was shown to remove
20 many metallic impurities of concern that may be present in gold. These impurities include Pt, Pd, Sn, Pb, Ag, Cu, Fe, Zn, Ni, and Al.

[00437] Table 5E: Summary of key impurities found in the gold used as feedstock for the above-described refining procedure.

Sample	Purity (%)	Gold Refining - Impurities Present in Gold (mg/kg)									
		Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Gold Head Sample	99.82%	4	29	19	4	569	864	28	175	16	20

[00438] Table 5F: Summary of key impurities removed from the gold in the key steps of the above-described refining process in milligrams per litre of solution.

Sample	Refining - Metals in Solution (mg/L)									
	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Leach	1	4	3	1	38	195	9	75	4	13
Post Reduction Filtrate	1	4	5	1	30	176	8	35	4	5
Thiourea Rinse	0	0	0	0	3	2	0	2	0	0

[00439] Table 5G: Summary of key impurities found in gold before and after the above-described refining process in milligrams per kilogram, carried out on gold. Analysis was performed in-house and by a Third Party for confirmation. The purity below is measured before the rinsing step of the procedure.

Sample	Purity (%)	Gold Refining - Impurities Present in Gold (mg/kg)									
		Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Head Sample (In-house Analysis)	99.82%	4	29	19	4	569	864	28	175	16	20
Refined (In-house Analysis)	99.994%	0	0	5	0	18	12	6	0	0	20
Refined (Third Party Analysis)	99.997%	0	0	4	0	21	0	3	0	0	1

[00440] Table 5H: Summary of key impurities found in gold before and after the above-described refining process in milligrams per kilogram, carried out on gold. Analysis was performed in-house and by a Third Party for confirmation. The purity below is measured after the rinsing step of the procedure.

Sample	Purity (%)	Gold Refining - Impurities Present in Gold (mg/kg)									
		Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Head Sample (In-house Analysis)	99.82%	4	29	19	4	569	864	28	175	16	20
Refined (In-house Analysis)	99.996%	0	0	5	0	4	6	7	0	0	17
Refined (Third Party Analysis)	99.998%	0	0	4	0	0	0	3	0	0	1

[00441] **Example 6** - Supplemental Examples of Refining Precious Metals Under Various Conditions

[00442] **Materials**

[00443] Chemicals

5 **[00444]** All chemicals in this study were purchased as reagent grade and used without further purification. Acids, solvents, salts, reducing agents, and oxidants including ultra-pure 37% HCl, ultra-pure 70% nitric acid, ammonium chloride, magnesium chloride, ascorbic acid, iron (III) chloride, thiourea, sodium metabisulfite, sodium thiosulfate, sodium sulfite, sodium hydroxide, and sodium chlorate were purchased from VWR and used as received. Glacial
10 acetic acid was purchased in bulk from Univar.

[00445] Equipment

[00446] For this study, all glassware, weigh boats, scoopulas, pipettes, and micropipette tips were taken from new stock and were both cleaned and stored separately from the rest of the laboratory equipment. Other necessary equipment used included magnetic stir plates,
15 Büchner funnels and flasks, and appropriate filter papers. Analysis was carried out using Thermo Scientific iCAP PRO XP Duo instrument, using ICP grade standards from Fisher Scientific.

[00447] **Analysis**

[00448] ICP-OES

20 **[00449]** Analysis was carried out in-house using the Thermo Scientific iCAP PRO XP Duo (ICP-OES) instrument. Standards and samples are diluted in approx. 3% HNO₃ solution using reverse-osmosis water to match the matrix of each sample being analyzed to the standards. Argon is used as both the cooling gas and carrier gas for this instrument. Quality control samples are analyzed approximately every 10-20 samples to observe possible
25 instrument drift and to ensure proper calibration.

[00450] **Feedstock**

[00451] The gold powder for use in these processes is obtained from e-waste.

[00452] **Experimental Methods**

[00453] General Chemical Processing Procedure

30 **[00454]** Gold powder obtained from various sources was leached using a lixiviant solution (otherwise referred to herein as the refining solution, or leaching mixture) containing appropriate amounts of solvent, oxidant, and ligand, stirring at 700 rpm at standard ambient temperature and pressure conditions for twenty minutes. The lixiviant solution was recharged

regularly as needed. After completion of the leach, the solution was filtered to separate the solid byproduct and the filtrate was analyzed by ICP-OES. Based on the gold content, a solution containing the appropriate amount of reducing agent was added to the filtrate and the reaction proceeded until the filtrate no longer contained gold, as analyzed by ICP-OES. The solution was then filtered to collect the gold, and then the solid powder was rinsed with a selection of solutions before drying. After drying, 0.1 g of the solid was treated with 20 mL of reverse aqua regia (three volumetric parts of conc. HNO_3 and one volumetric part of conc. HCl) for 20 minutes to complete dissolution of the solid. This solution was then diluted and analyzed by ICP-OES to determine purity.

10 **[00455] Selected Examples of Chemical Processing**

[00456] Reducing Agents

[00457] Sodium Metabisulfite

[00458] 150 mL of a 0.5 mol/L HCl solution was prepared in a 400 mL beaker fitted with an appropriately sized stir bar. Subsequently, 30 g of e-waste gold was added to this beaker and rinsed with stirring at approx. 700 rpm in this solution for 10 minutes. After 10 minutes, the stirring was stopped, and the gold was allowed to settle. Once settled, an aliquot was removed for analysis by ICP-OES and then the solution was decanted. The gold was then washed with 150 mL and 60 mL of distilled *water* and *glacial acetic acid* respectively. After each rinse, the solution was allowed to settle, sampled for analysis by ICP-OES, and decanted.

20 **[00459]** A leach solution was prepared in another 400 mL beaker by mixing 90 mL *glacial acetic acid*, 60 mL concentrated HCl , and 7.5 g MgCl_2 . After allowing the MgCl_2 to slightly dissolve, an initial volume of 5 mL NaClO_3 solution (40% w/w) was slowly added to the solution, followed immediately by all the previously rinsed gold. The leach solution was dosed with another 5 mL NaClO_3 solution at 3 and 6 minutes before allowing the reaction to proceed for 15 minutes to leach all the gold.

25 **[00460]** Once the leach was completed, the solution was vacuum filtered, and the filtrate collected in a third 400 mL beaker with a stir bar. An aliquot was removed for analysis by ICP-OES. To this beaker, a solution of 60 g *sodium metabisulfite* in 91.9 mL *water* was slowly added. Once the entire volume of this solution was added, the reaction was allowed to proceed for 20 minutes. After 20 minutes, an aliquot was removed and centrifuged such that the filtrate could be sampled for analysis by ICP-OES. Once the analysis of this filtrate read <10 mg/L gold in solution, it could be filtered by vacuum. If there was still >10 mg/L gold in solution, the

reaction was allowed to proceed and sampled every 10 minutes until the filtrate reads <10 mg/L gold.

5 [00461] After the filtration of the gold solution, the vacuum flask was replaced and 150 mL of *water* was poured over the gold cake, and approx. 10 mL *water* was used to rinse out the reaction vessel. Once the filtration was complete, a second measure of 150 mL of *water* was poured over the cake. In parallel, 150 mL of a 0.5 M *HCl* and 1 M *thiourea* solution was prepared in a 400 mL beaker with a stir bar. Once the *thiourea* was dissolved, the gold was removed from the Büchner funnel and added to the beaker to be rinsed in this solution for 10 minutes. After 10 minutes, the stirring was stopped, and the gold was allowed to settle. Once settled, an aliquot was removed for analysis by ICP-OES and then the solution was decanted. 10 The gold was then washed with 150 mL of *water*, twice. After each rinse, the solution was allowed to settle, sampled for analysis by ICP-OES, and decanted.

[00462] The gold was briefly rinsed with *methanol* to expedite drying. This *methanol* was decanted and then the gold dried on a hot plate at 110°C. Upon drying, 0.1 g of the gold was removed for digestion with reverse aqua regia for 20 minutes, allowed to degas and then dilutions of 2, 10 and 1000 times were prepared for analysis by ICP-OES. 15

[00463] Sodium Sulfite

[00464] 27.5 mL of a 1 mol/L *thiourea* solution was prepared in a 40 mL vial fitted with an appropriately sized stir bar. Subsequently, 5.5 g of e-waste gold was added to this beaker and rinsed with stirring at approx. 700 rpm in this solution for 10 minutes. After 10 minutes, the stirring was stopped, and the gold allowed to settle. Once settled, an aliquot was removed for analysis by ICP-OES and then the solution was decanted. The gold was then washed with 27.5 mL and 11 mL of distilled *water* and *glacial acetic acid* respectively. After each rinse, the solution was allowed to settle, sampled for analysis by ICP-OES, and decanted. 20

25 [00465] A leach solution was prepared in a clean 40 mL vial by mixing the previously rinsed 5.5 g powdered gold, 16.5 mL *glacial acetic acid*, and 11.0 mL concentrated *HCl*. After allowing the solution to homogenize, an initial volume of 0.92 mL *NaClO₃* solution (40% w/w) was added to the solution. The leach solution was dosed with another 0.92 mL *NaClO₃* solution at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes to leach all the gold.

30 [00466] Once the leach was completed, the solution was centrifuged, decanted, and the filtrate was collected in a clean 40 mL vial with a stir bar. An aliquot was removed for analysis by ICP-OES. 15.0 mL of this leach solution was added to a clean 40 mL vial with a stir bar. To this vial, a solution of 3 g *sodium sulfite* in 9 mL hot *water* was added. Once the entire volume

of this solution was added, the reaction was allowed to proceed for 10 minutes. After 10 minutes, 0.72 g *NaOH* in 3.6 mL *water* was added to the vial, and the reaction was allowed to proceed for an additional 10 minutes. After a total elapsed time of 20 minutes, another 0.72 g *NaOH* in 3.6 mL *water* was added to the vial, and the reaction proceeded for an additional 20 minutes. After this elapsed time of 40 minutes, an aliquot was removed and centrifuged such that the filtrate could be sampled for analysis by ICP-OES. At this point the filtrate read 11 mg/L gold in solution, and it was centrifuged and decanted.

[00467] After the centrifugation and decanting of the reduction filtrate, the gold solid was washed with 25 mL of *water*. Once centrifuged and decanted, the gold was washed with a second measure of 25 mL of *water*. In parallel, 12.5 mL of a 0.5 M *HCl* and 1 M *thiourea* solution was prepared in a 40 mL vial with a stir bar. Once the *thiourea* was dissolved, the *thiourea* solution was added to the gold-containing vial and the gold was washed for 10 minutes. After 10 minutes, the stirring was stopped, and the gold was centrifuged. Once centrifuged, an aliquot was removed for analysis by ICP-OES and then the solution was decanted. The gold was then washed with 3 measures of 12.5 mL of room temperature *water*. After each rinse, the solution was centrifuged, sampled for analysis by ICP-OES, and decanted.

[00468] The gold was briefly rinsed with *methanol* to expedite drying. This *methanol* was decanted and then the gold dried on a hot plate at 110°C. Upon drying, 0.1 g of the gold was removed for digestion with reverse aqua regia for 20 minutes, allowed to degas and then dilutions of 2, 10 and 1000 times were prepared for analysis by ICP-OES.

[00469] Thiourea

[00470] A leach solution was prepared in a new 40 mL vial by mixing 5.5 g powdered gold, 16.5 mL *glacial acetic acid*, and 11.0 mL concentrated *HCl*. After allowing the solution to homogenize, an initial volume of 0.92 mL *NaClO₃* solution (40% w/w) was added to the solution. The leach solution was dosed with another 0.92 mL *NaClO₃* solution at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes to leach all the gold.

[00471] Once the leach was completed, the solution was centrifuged, decanted, and the filtrate was collected in a new 40 mL vial with a stir bar. An aliquot was removed for analysis by ICP-OES. 15.0 mL of this leach solution was added to a new 40 mL vial with a stir bar. To this vial, a solution of 0.51 g *thiourea* in 3.6 mL *water* was added. Once the entire volume of this solution was added, the reaction was allowed to proceed for 10 minutes. After 10 minutes, 0.72 g *NaOH* in 3.6 mL *water* was added to the vial, and the reaction was allowed to proceed

for an additional 10 minutes. After a total elapsed time of 20 minutes, another 0.72 g *NaOH* in 3.6 mL *water* was added to the vial, and the reaction proceeded for an additional 20 minutes. After this elapsed time of 40 minutes, an aliquot was removed and centrifuged such that the filtrate could be sampled for analysis by ICP-OES. At this point the filtrate read <5000 mg/L gold in solution, and could be centrifuged and decanted. This still pregnant solution was set aside for later precipitation and the resulting gold may be recirculated into the refining cycle.

[00472] After the centrifugation and decanting of the gold solution, the gold solid was washed with 25 mL of *water*. Once centrifuged and decanted, the gold was washed with a second measure of 25 mL of *water*. In parallel, 12.5 mL of a 0.5 M *HCl* and 1 M *thiourea* solution was prepared in a 40 mL vial with a stir bar. Once the *thiourea* was dissolved, the *thiourea* solution was added to the gold-containing vial and the gold was washed for 10 minutes. After 10 minutes, the stirring was stopped, and the gold was centrifuged. Once centrifuged, an aliquot was removed for analysis by ICP-OES and then the solution was decanted. The gold was then washed with 3 measures of 12.5 mL of room temperature *water*. After each rinse, the solution was centrifuged, sampled for analysis by ICP-OES, and decanted.

[00473] The gold was briefly rinsed with *methanol* to expedite drying. This *methanol* was decanted and then the gold dried on a hot plate at 110°C. Upon drying, 0.1 g of the gold was removed for digestion with reverse aqua regia for 20 minutes, allowed to degas and then dilutions of 2, 10 and 1000 times were prepared for analysis by ICP-OES.

[00474]

[00475] A leach solution was prepared in a new 40 mL vial by mixing 4.5 g powdered gold, 13.5 mL *glacial acetic acid*, and 9.0 mL concentrated *HCl*. After allowing the solution to homogenize, an initial volume of 0.75 mL *NaClO₃* solution (40% w/w) was added to the solution. The leach solution was dosed with another 0.75 mL *NaClO₃* solution at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes to leach all the gold.

[00476] Once the leach was completed, the solution was centrifuged, decanted, and the filtrate was collected in a new 40 mL vial with a stir bar. An aliquot was removed for analysis by ICP-OES. 10.0 mL of this leach solution was added to a new 40 mL vial with a stir bar. This vial was placed into a pre-prepared hot water bath set to 60°C. To this vial, a solution of 0.363 g *thiourea* in 2.56 mL *water* was added. Once the entire volume of this solution was added, the reaction was allowed to proceed for 90 minutes. After this elapsed time of 90 minutes, an aliquot was removed and centrifuged such that the filtrate could be sampled for analysis by

ICP-OES. At this point the filtrate read <2000 mg/L gold in solution, and could be centrifuged and decanted. This still pregnant solution was set aside for later precipitation and the resulting gold could be recirculated into the refining cycle.

[00477] After the centrifugation and decanting of the gold solution, the gold solid was washed with 25 mL of *water*. Once centrifuged and decanted, the gold was washed with a second measure of 25 mL of *water*. In parallel, 12.5 mL of a 0.5 M *HCl* and 1 M *thiourea* solution was prepared in a 40 mL vial with a stir bar. Once the *thiourea* was dissolved, the *thiourea* solution was added to the gold-containing vial and the gold was washed for 10 minutes. After 10 minutes, the stirring was stopped, and the gold was centrifuged. Once centrifuged, an aliquot was removed for analysis by ICP-OES and then the solution was decanted. The gold was then washed with 3 measures of 12.5 mL of room temperature *water*. After each rinse, the solution was centrifuged, sampled for analysis by ICP-OES, and decanted.

[00478] The gold was briefly rinsed with *methanol* to expedite drying. This *methanol* was decanted and then the gold dried on a hot plate at 110°C. Upon drying, 0.1 g of the gold was removed for digestion with reverse aqua regia for 20 minutes, allowed to degas and then dilutions of 2, 10 and 1000 times were prepared for analysis by ICP-OES.

[00479] A leach solution was prepared in a new 40 mL vial by mixing 4.5 g powdered gold, 3.6 mL *water*, 6.8 mL *glacial acetic acid*, and 9.9 mL concentrated *HCl*. After allowing the solution to homogenize, an initial volume of 0.75 mL *NaClO₃* solution (40% w/w) was added to the solution. The leach solution was dosed with another 0.75 mL *NaClO₃* solution at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes to leach all the gold.

[00480] Once the leach was completed, the solution was centrifuged, decanted, and the filtrate was collected in a new 40 mL vial with a stir bar. An aliquot was removed for analysis by ICP-OES. 10.0 mL of this leach solution was added to a new 40 mL vial with a stir bar. This vial was placed into a pre-prepared hot water bath set to 60°C. To this vial, a solution of 0.40 g *thiourea* in 2.82 mL *water* was added. Once the entire volume of this solution was added, the reaction was allowed to proceed for 90 minutes. After this elapsed time of 90 minutes, an aliquot was removed and centrifuged such that the filtrate could be sampled for analysis by ICP-OES. At this point the filtrate read <500 mg/L gold in solution, and could be centrifuged and decanted.

[00481] After the centrifugation and decanting of the reduction filtrate, the gold solid was washed with 10 mL of *water*. Once centrifuged and decanted, the gold was washed with a second measure of 10 mL of *water*. In parallel, 17.5 mL of a 0.5 M *HCl* and 1 M *thiourea* solution was prepared in a 40 mL vial with a stir bar (Large volume because the gold from 4 identical experiments carried out in tandem was combined). Once the *thiourea* was dissolved, the *thiourea* solution was added to the gold-containing vial and the gold was washed for 10 minutes. After 10 minutes, the stirring was stopped, and the gold was centrifuged. Once centrifuged, an aliquot was removed for analysis by ICP-OES and then the solution was decanted. The gold was then washed with 2 measures of 10 mL of room temperature *water*. After each rinse, the solution was centrifuged, sampled for analysis by ICP-OES, and decanted.

[00482] The gold was briefly rinsed with *methanol* to expedite drying. This *methanol* was decanted and then the gold dried on a hot plate at 110°C. Upon drying, 0.5 g of the gold was removed for digestion with reverse aqua regia for 20 minutes, allowed to degas and then dilutions of 10, 100 and 10000 times were prepared for analysis by ICP-OES.

[00483] **Water Content**

[00484] Beyond the original leach solvent which only used glacial acetic acid as a solvent (and equated to 55% by volume), experiments were carried out with varying amount of water substituted for a portion of the solvent to see how effective the leach and refining process would be in the presence of water. In this section, only the leach portion of the refining process is described. This is because if the leach does not completely digest the gold, there was little use in carrying it through the whole reducing and rinsing procedure.

[00485] 0% Glacial acetic acid by volume

[00486] A 10:1 phase ratio leach solution was prepared in a clean 40 mL vial by mixing 1 g powdered gold, 7.5 mL *water*, and 2 mL concentrated *HCl*. After allowing the solution to homogenize, an initial volume of 0.167 mL *NaClO₃* solution (40% w/w) was added to the solution. The leach solution was dosed with another 0.167 mL *NaClO₃* solution at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes. Once these 10 minutes had elapsed, almost all the gold remained in the vial and this experiment was abandoned.

[00487] A 5:1 phase ratio leach was prepared in a clean 40 mL vial by mixing 1 g powdered gold, 3 mL *water*, and 2 mL concentrated *HCl*. After allowing the solution to

homogenize, an initial volume of 0.167 mL NaClO_3 solution (40% w/w) was added to the solution. The leach solution was dosed with another 0.167 mL NaClO_3 solution at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes before sampling. Once these 10 minutes had elapsed, a significant amount of gold remained in the vial, so it was allowed to keep stirring and sampled at 20 and 95 minutes. After this time, there was still approximately half of the gold remaining and this experiment was abandoned.

[00488] 5% Glacial acetic acid by volume

[00489] A 10:1 phase ratio leach solution was prepared in a clean 40 mL vial by mixing 1 g powdered gold, 7 mL water, 0.5 mL glacial acetic acid, and 2 mL concentrated HCl . After allowing the solution to homogenize, an initial volume of 0.167 mL NaClO_3 solution (40% w/w) was added to the solution. The leach solution was dosed with another 0.167 mL NaClO_3 solution at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes. Once these 10 minutes had elapsed, almost all the gold remained in the vial and this experiment was abandoned.

15 [00490] 10% Glacial acetic acid by volume

[00491] A 5.3:1 phase ratio leach was prepared in a clean 40 mL vial by mixing 1 g powdered gold, 2.5 mL water, 0.5 mL glacial acetic acid and 2 mL concentrated HCl . After allowing the solution to homogenize, an initial volume of 0.167 mL NaClO_3 solution (40% w/w) was added to the solution. The leach solution was dosed with another 0.167 mL NaClO_3 solution at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes before sampling. Once these 10 minutes had elapsed, approximately half of the gold remained, and the solution was allowed to continue to stir until 95 minutes. After this time, there was still approximately one quarter of the gold remaining and this experiment was abandoned.

[00492] 20% Glacial acetic acid by volume

25 [00493] A 10:1 phase ratio leach solution was prepared in a clean 40 mL vial by mixing 1 g powdered gold, 5.5 mL water, 2 mL glacial acetic acid, and 2 mL concentrated HCl . After allowing the solution to homogenize, an initial volume of 0.167 mL NaClO_3 solution (40% w/w) was added to the solution. The leach solution was dosed with another 0.167 mL NaClO_3 solution at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes. Once these 30 10 minutes had elapsed, almost all the gold remained in the vial. It was allowed to continue stirring for an additional half hour, and sampled. There was no significant improvement and thus this experiment was abandoned.

- [00494] A 5.6:1 phase ratio leach solution was prepared in a clean 40 mL vial by mixing 1 g powdered gold, 2 mL *water*, 1 mL *glacial acetic acid*, and 2 mL concentrated *HCl*. After allowing the solution to homogenize, an initial volume of 0.167 mL *NaClO₃ solution* (40% w/w) was added to the solution. The leach solution was dosed with another 0.167 mL *NaClO₃ solution* at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes. Once these 10 minutes had elapsed, more than half of the gold was leached so it was allowed to stir for an additional 10 minutes before being dosed with 0.083 mL *NaClO₃ solution*, and after 10 more minutes of agitation there was no significant improvement and thus this experiment was abandoned.
- 10 [00495] 30% Glacial acetic acid by volume
- [00496] A 6:1 phase ratio leach solution was prepared in a clean 40 mL vial by mixing 1 g powdered gold, 1.5 mL *water*, 1.8 mL *glacial acetic acid*, and 2 mL concentrated *HCl*. After allowing the solution to homogenize, an initial volume of 0.167 mL *NaClO₃ solution* (40% w/w) was added to the solution. The leach solution was dosed with another 0.167 mL *NaClO₃ solution* at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes. Once these 15 10 minutes had elapsed, more than 80% of the gold was leached so it was allowed to stir for an additional 10 minutes before being dosed with 0.083 mL *NaClO₃ solution*; and after 10 more minutes of agitation, another 0.167 mL *NaClO₃ solution* was added and allowed to stir for 10 more minutes and sampled. Almost all the gold was leached after this time period and dosing regime.
- 20 [00497] In view of the success of the 30% *glacial acetic acid* recipe, some minor adjustments were made. A 5:1 phase ratio leach solution was prepared in a clean 40 mL vial by mixing 2 g powdered gold, 1.6 mL *water*, 3 mL *glacial acetic acid*, and 4.4 mL concentrated *HCl*. After allowing the solution to homogenize, an initial volume of 0.33 mL *NaClO₃ solution* (40% w/w) was added to the solution. The leach solution was dosed with another 0.33 mL *NaClO₃ solution* at 1 and 2 minutes before allowing the reaction to proceed for 10 minutes. Once these 10 minutes had elapsed a small amount of gold remained visible, and the solution was allowed to continue stirring for an additional 10 minutes.
- 25 [00498] This selection of experiments informed the herein described refining solution having a 5:1 phase ratio of 30% by volume *glacial acetic acid*.
- 30

[00499] Dosing Regimes

[00500] Different oxidant dosing regimes were tested, including discrete manual dosing and continuous dosing using dosing pumps. In this section, only the leach portion of the refining chemistry will be discussed as it is the primary step affected by the dosing of oxidant. In this section, oxidant dosing of the 55% *glacial acetic acid* by volume recipe is presented.

[00501] Dosing pump – 5-minute continuous dosing

[00502] A refining solution was prepared in a clean 80 mL beaker by mixing 10 g powdered gold, 30 mL *glacial acetic acid* and 20 mL *concentrated HCl*. This solution was stirred with a magnetic stir bar on a stirring plate at room temperature and once homogenized, a dosing pump with a syringe containing NaClO_3 solution (40% w/w) was used to dose 5 mL of NaClO_3 solution at a rate of 1 mL/min into the beaker. After the dosing was complete, the solution was stirred for an additional 15 minutes until all the gold powder was leached and the leach solution was bright orange. The solution was filtered, sampled for ICP-OES analysis and carried through to the gold reduction stage. This dosing regime is also represented on a large scale below at second 'Scale Up - System Described herein), with the 30% *glacial acetic acid* by volume recipe.

[00503] Discrete Dosing – Every 3 minutes

[00504] A refining solution was prepared in a clean 80 mL beaker by mixing 30 mL *glacial acetic acid*, 20 mL *concentrated HCl*, and 5 g MgCl_2 . This solution was stirred with a magnetic stir bar on a stirring plate at room temperature to dissolve the MgCl_2 , then 10 g of powdered gold was added to the beaker, and once homogenized, an initial volume of 1.66 mL NaClO_3 solution (40% w/w) was added to the solution. The leach solution was dosed with another 1.66 mL NaClO_3 solution at 3 and 6 minutes before allowing the reaction to proceed for 9 minutes to leach all the gold. The solution was filtered, sampled for ICP-OES analysis and carried through to the gold reduction stage.

[00505] Discrete Dosing – Every 1 minute

[00506] A refining solution was prepared in a clean 200 mL beaker by mixing 20 g powdered gold, 60 mL *glacial acetic acid*, and 40 mL *concentrated HCl*. This solution was stirred with a magnetic stir bar on a stirring plate at room temperature and once homogenized, an initial volume of 3.34 mL NaClO_3 solution (40% w/w) was added to the solution. The leach solution was dosed with another 3.34 mL NaClO_3 solution at 1 and 2 minutes before allowing the reaction to proceed for 25 minutes to leach all the gold. The solution was filtered, sampled for ICP-OES analysis and carried through to the gold reduction stage.

[00507] Rinsing

[00508] Several rinses were tested when developing there herein described refining methods. In this section, individual rinse procedures will be discussed, separating them from the refining methods.

[00509] Hot HCl Rinse

[00510] To prepare a 3M *HCl* rinse, 7.87 mL concentrated *HCl* was added to 23.63 mL *water*. This solution was well mixed and then added to a vial containing 3.2 g of powdered gold. This vial was placed on a stirring hot plate set to heat the mixture to 50°C, and then the gold was agitated in this vessel at this temperature for 30 minutes. Once the 30 minutes had elapsed, the vial was centrifuged, the rinse decanted, and the gold rinsed with water before drying.

[00511] Hot HNO₃ Rinse

[00512] To prepare a 3M *HNO₃* rinse, 5.31 mL concentrated *HNO₃* was added to 22.69 mL *water*. This solution was well mixed and then added to a vial containing 3.2 g of powdered gold. This vial was placed on a stirring hot plate set to heat the mixture to 50°C, and then the gold was agitated in this vessel at this temperature for 30 minutes. Once the 30 minutes had elapsed, the vial was centrifuged, the rinse decanted, and the gold rinsed with water before drying.

[00513] Room Temperature HCl Rinse

[00514] To prepare a 0.5M *HCl* rinse, 0.83 mL of concentrated *HCl* was added to 19.17 mL *water*. This solution was well mixed and then added to a vial containing 2 g of powdered gold. This vial was placed on a stir plate, and then the gold was agitated in this vessel at room temperature for 10 minutes. Once the 10 minutes had elapsed, the vial was centrifuged, the rinse decanted, and the gold rinsed with water before drying.

[00515] Thiourea Rinse

[00516] To prepare a 1M *thiourea* rinse, 1.52 g *thiourea* was added to 20 mL *water*. Once dissolved, this solution was added to a vial containing 2 g of powdered gold. This vial was placed on a stir plate, and then the gold was agitated in this vessel at room temperature for 10 minutes. Once the 10 minutes had elapsed, the vial was centrifuged, the rinse decanted, and the gold rinsed with water before drying.

[00517] Thiourea/HCl Rinse

[00518] To prepare a 1M *thiourea* and 0.5M *HCl* rinse, 0.76 g *thiourea* was dissolved in 9.58 mL *water*, and once this was dissolved, 0.42 mL concentrated *HCl* was added to this mixture and well combined. This was then added to a vial containing 2 g powdered gold. This vial was placed on a stir plate, and then the gold was agitated in this vessel at room temperature for 10 minutes. Once the 10 minutes had elapsed, the vial was centrifuged, the rinse decanted, and the gold rinsed with water before drying.

[00519] Sodium Thiosulfate Rinse

[00520] To prepare a 1.5M *sodium thiosulfate* rinse, 2.37 g *sodium thiosulfate* was dissolved in 10 mL *water* and then added to a vial containing 2 g powdered gold. This vial was placed on a stir plate, and then the gold was agitated in this vessel at room temperature for 30 minutes. Once the 30 minutes had elapsed, the vial was centrifuged, the rinse decanted, and the gold rinsed with water before drying.

[00521] **Temperature Testing**

15 [00522] To assess a temperature at which to carry out gold reduction from a kinetics standpoint, a series of tests were carried out.

[00523] A refining solution was prepared in a clean 80 mL beaker by mixing 12 g powdered gold, 36 mL *glacial acetic acid*, and 24 mL concentrated *HCl*. After allowing the solution to homogenize, an initial volume of 2 mL *NaClO₃* solution (40% w/w) was added to the solution. The leach solution was dosed with another 2 mL *NaClO₃* solution at 1 and 2 minutes before allowing the reaction to proceed for 15 minutes to leach all the gold.

[00524] Once the leach was completed, the solution was filtered and sampled. Four aliquots of 10 mL of this filtrate were taken and placed into four separate clean 40 mL vials equipped with a stir bar. The first vial was placed on a stir plate and left at room temperature. 25 The second was placed into a 60°C hot water bath on a stirring hot plate. The third was placed into a 45°C hot water bath on a stirring hot plate. The last vial was placed into an ice bath on a stir plate. To each vial, 2.56 mL of saturated *thiourea* solution (0.142 g/mL) was added, and the vials were stirred to react for 20 minutes at their respective temperatures. After 20 minutes, each vial was removed from stirring and centrifuged to sample for ICP-OES analysis. The vials 30 were returned to their respective stir plates and the reactions continued for an additional 20 minutes. This sampling was repeated at 40, 60 and 120 minutes.

[00525] After 120 minutes, the vials were set aside to recover the gold later. The purity assessments were not carried out as the objective of this series of experiments was to determine the best reduction conditions.

5 [00526] To confirm results, the 60°C reduction was carried out in quadruplicate with the 55% by volume *glacial acetic acid* recipe, as well as in quadruplicate with the 30% by volume *glacial acetic acid* recipe, to test the procedure for both.

[00527] For the **55% by volume *glacial acetic acid* recipe**, a leaching mixture was prepared in a clean 40 mL vial by mixing 4.5 g powdered gold, 13.5 mL *glacial acetic acid*, and 9 mL concentrated *HCl*. After allowing the solution to homogenize, an initial volume of 0.75 mL
10 *NaClO₃* solution (40% w/w) was added to the solution. The leach solution was dosed with another 0.75 mL *NaClO₃* solution at 1 and 2 minutes before allowing the reaction to proceed for 15 minutes to leach all the gold.

[00528] Once the leach was completed, the solution was centrifuged and sampled. The leach solution was decanted into a clean 40 mL vial. Four aliquots of 10 mL of this filtrate were
15 taken and placed into four separate clean 40 mL vials equipped with a stir bar. Each vial was placed into 60°C hot water baths on stirring hot plates. Each vial was dosed with 2.56 mL of saturated *thiourea* solution (0.142 g/mL) was added, and the vials were stirred to react for 60 minutes at their respective temperatures. After 60 minutes, each vial was removed from stirring and centrifuged to sample for ICP-OES analysis. The vials were returned to their respective
20 stir plates and the reactions continued for an additional 30 minutes.

[00529] After 90 minutes, the vials were set aside to recover the gold later. The purity assessments were not carried out as the priority of this series of experiments was to determine the best reduction conditions.

[00530] For the **30% by volume *glacial acetic acid* recipe**, a leach was prepared in a
25 clean 40 mL vial by mixing 4.5 g powdered gold, 3.6 mL *water*, 6.8 mL *glacial acetic acid*, and 9.9 mL concentrated *HCl*. After allowing the solution to homogenize, an initial volume of 0.75 mL *NaClO₃* solution (40% w/w) was added to the solution. The leach solution was dosed with another 0.75 mL *NaClO₃* solution at 1 and 2 minutes before allowing the reaction to proceed for 15 minutes to leach all the gold.

30 [00531] Once the leach was completed, the solution was centrifuged and sampled. The leach was decanted into a clean 40 mL vial. Four aliquots of 10 mL of this filtrate were taken and placed into four separate clean 40 mL vials equipped with a stir bar. Each vial was placed into 60°C hot water baths on stirring hot plates. Each vial was dosed with 2.82 mL of saturated

thiourea solution (0.142 g/mL) was added, and the vials were stirred to react for 60 minutes at their respective temperatures. After 60 minutes, each vial was removed from stirring and centrifuged to sample for ICP-OES analysis. The vials were returned to their respective stir plates and the reactions continued for an additional 30 minutes.

- 5 [00532] After 90 minutes, the vials were set aside to recover the gold later. The purity assessments were not carried out as the objective of this series of experiments was to determine the best reduction conditions.

[00533] **Scale Up – System Described Herein**

- 10 [00534] Lab scale experiments ranged from 1 g to 57 g input gold, and this data was collected and used to inform the development of a refining system with a capacity of up to 500 g gold per run. Described here is a run in this refining system (for more details, see Example 7), with a gold loading of 420 g. All chemicals and solutions described here are pumped into respective reactors using dosing pumps.

- 15 [00535] **Thiourea solution preparation:**

- [00536] A saturated solution (0.142 g/mL) of *thiourea* was prepared in a 20 L jacketed reactor by pumping in 2500 mL *water* into it, and then adding 355 g of *thiourea*. This solution was stirred with an overhead agitator for 60 minutes at 30°C until the *thiourea* solid dissolved, and then the solution was kept at this temperature until needed in the refining process to
20 ensure that solids would not drop out.

[00537] **Leach Preparation:**

- [00538] A refining solution was prepared in a 5 L reactor by pumping in 338 mL *water*, followed by 628 mL *glacial acetic acid*, and then 924 mL concentrate *HCl*. The overhead agitator in this reactor was turned on to homogenize this mixture. Upon mixing, 420 g of
25 powdered gold was added into the reactor. Once the powdered gold was well combined in the solution, dosing of NaClO_3 solution (40% w/w) began. This solution was dosed at 42 mL/min for 5 minutes, totalling an added volume of 210 mL. The leach reaction took place over 10 minutes when no visible gold remained in solution and then the solution was sampled for ICP-OES analysis from the top through a sampling tube. Following this sample, the gold containing
30 leach solution was pumped through a cartridge filter into a 5 L reduction reactor equipped with a heating belt. 250 mL *glacial acetic acid* was dosed into the original leach reactor and pumped through the lines and cartridge filter to bring over any remaining leach solution that was still held in the lines.

[00539] Gold Reduction:

[00540] The gold-containing leached solution that was pumped over to the reduction reactor was stirred using an overhead agitator and then 592 mL of the pre-prepared saturated *thiourea* solution was dosed into the reactor. Once the *thiourea* solution was added in, the heating belt was set to 63°C and the whole solution was agitated at this temperature for 60 minutes. After 60 minutes, agitation was stopped, the gold allowed to settle, and the solution was sampled for ICP-OES analysis from the top using a sampling tube, and then the solution was filtered through the bottom filter in the reactor, kidney looped back through the reactor for 10 minutes and then fully filtered through the bottom filter, a polishing cartridge filter and then pumped into a container for storage or disposal. A kidney loop may be used to reduce or prevent loss of leached solution before reduction begins in dead zones, cavities, or voids within a reactor. If any such leached solution is collected in said dead zones, etc., the kidney loop feeds that leached solution back into the reactor to be contacted with the reductant. Absent a kidney loop, there may be a potential, small loss of gold - but such a loss would not be expected to affect final purity. Once the reduction filtrate was completely removed, all that remained in the reactor was refined powdered gold. The heating belt was turned off.

[00541] To this reactor, 2.1 L of *water* was pumped in, and agitation started, to stir and rinse the gold for 2 minutes. After 2 minutes, this *water* rinse was filtered out into an aqueous waste container. Next, the *thiourea* and *HCl* rinse was prepared in the reactor on top of the gold by pumping in 883 mL *water*, starting agitation, then pumping in 1129 mL pre-prepared saturated *thiourea* solution, followed by 88 mL of concentrated *HCl*. This rinse and the gold were agitated for 10 minutes. After 10 minutes, agitation was stopped, the gold allowed to settle, the rinse sampled from the top for ICP-OES analysis and then the rinse was filtered out into the aqueous waste container. Once more, 2.1 L *water* was pumped into the reactor, the agitation turned on, the gold rinsed one final time for 2 minutes, and then the agitation was turned off, the gold allowed to settle, and the *water* rinse pumped and filtered out into the aqueous waste container.

[00542] This reduction reactor has a removable filter bottom, so this was unlatched and the gold cake removed from the reactor and placed onto a hot plate to dry. Once dry, the gold was removed from the filter into a clean container, mixed well, and then 0.5 g of the gold was removed for a purity analysis by digesting it in 20 mL of reverse-aqua regia.

[00543] RESULTS & DISCUSSION

[00544] A note on purity discussions carried out in the following section. The analysis of the initial samples is carried out in-house, while the analysis of the final gold samples is carried out both in-house and by a Third Party. This makes it difficult to directly compare the values provided for the initial feed and the purity analysis from the Third Party, but it provides a good comparison.

[00545] The results of the ICP-OES analysis were used to track the removal of metals from the gold solid or gold-containing lixiviant (refining) solution. For gold numbers and metal accountability, it should be noted that the high mg/L of Au in solution approaches or even exceeds the high end of the sensitivity of the standards used with the ICP-OES instrument. It is likely that the numbers over 100000 mg/L may be under reported by the ICP-OES. For complete leaching assessment, visual confirmations are used.

[00546] **Reducing Agents**

[00547] Several reducing agents were considered in the development of this refining methodology. Here, a comparison between *sodium metabisulfite*, *sodium sulfite* and *thiourea* will be discussed. Section "Example 6 - **Selected Examples of Chemical Processing - Reducing Agents**" describes the methods carried out in order to obtain the following results

[00548] Table 6A below shows the metals present in the refining solution post-leach, or dissolution of the gold, and in the post-reduction filtrate when dosed with *sodium metabisulfite* and allowed to react. This reducing agent was effective in the reduction of gold, only leaving 2 mg/L Au in solution, but it also had an effect on the other metals in solution. Ag is a primary impurity of concern in the refining of gold, and the observed drop in concentration from 36 mg/L to 7 mg/L is more than the expected drop in view of the dilution when the *sodium metabisulfite* is added as a saturated aqueous solution. Thus, it was observed that *sodium metabisulfite* also reduced Ag along with Au.

[00549] Table 6A: Summary of metals present in solution before and after gold reduction, using sodium metabisulfite as a reducing agent. Numbers displayed in mg/L.

	E-waste Gold Refining - <i>Sodium Metabisulfite</i> Reduction - Metals in Solution (mg/L)										
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Leach	131414	0	1	21	12	36	16	10	62	1	21
Post Reduction Filtrate	2	0	0	12	1	7	9	5	6	0	8

[00550] Table 6B below shows the metals present in the refining solution post-leach, or dissolution of the gold, and in the post-reduction filtrate when dosed with *sodium sulfite* and

allowed to react. It should be noted that in this reduction, *NaOH* was also dosed, as in some early iterations of the *thiourea* reduction chemistry (see below), to increase the kinetics of the reduction. This reducing agent was effective in the reduction of gold, only leaving 4 mg/L Au in solution, but it also influenced other metals in solution. Again, Ag is a primary impurity of concern in the refining of gold, and the observed drop from 15 mg/L to 0 mg/L is even more than the expected drop in view of dilution when the *sodium sulfite* is added as a saturated aqueous solution, as well as the addition of *NaOH* in an aqueous solution. Thus, it was observed that *sodium sulfite* also reduced Ag along with Au.

[00551] Table 6B: Summary of metals present in solution before and after gold reduction, using sodium sulfite as a reducing agent. Numbers displayed in mg/L.

	E-waste Gold Refining - <i>Sodium Sulfite</i> Reduction - Metals in Solution (mg/L)										
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Leach	142014	0	2	25	10	15	12	11	12	2	17
Post Reduction Filtrate	4	0	2	12	5	0	6	4	15	1	10

[00552] Table 6C below shows the metals present in the refining solution post-leach, or dissolution of the gold, and in the post-reduction filtrate when dosed with *thiourea* and allowed to react. It should be noted that in this reduction, *NaOH* was also dosed to increase the kinetics of the reduction. This is an optional step, and in some embodiments of the refining methods described herein, no *NaOH* is used at all. In this iteration of the *thiourea* chemistry, the design of the reduction left 4962 mg/L Au in solution, which equates to the effective reduction of 95% of the Au in solution. However, the other metals of concern remained in solution and thus were largely unaffected by the *thiourea*, even in view of the expected drop due to dilution when the *thiourea* is added as a saturated aqueous solution, as well as the addition of *NaOH* in an aqueous solution.

[00553] Table 6C: Summary of metals present in solution before and after gold reduction, using thiourea as a reducing agent (Thiourea 1). Numbers displayed in mg/L.

	E-waste Gold Refining - Thiourea Reduction - Metals in Solution (mg/L)										
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Leach	159162	0	2	58	237	28	18	46	12	2	39
Post Reduction Filtrate	4962	0	2	41	126	21	10	26	25	1	22

[00554] As noted above, through continued development of the herein described refining methodologies, it was determined that the dosing of NaOH was not required to assist the kinetics of the reduction but rather this could be achieved by carrying out the reduction at a higher temperature. One such way to do this is in a hot water bath.

- 5 **[00555]** Table 6D below shows the metals present in the refining solution post-leach, or dissolution of the gold, and in the post-reduction filtrate when dosed with *thiourea* and allowed to react. This reduction was carried out in a hot water bath at 60°C. Here, the *thiourea* was able to reduce 99% of the Au in solution. In addition to this improvement in the reduction, the remainder of the metal impurities in the solution remain untouched.

- 10 **[00556]** Table 6D: Summary of metals present in solution before and after gold reduction, using thiourea as a reducing agent (Thiourea 2), reduction carried out in a hot water bath. Numbers displayed in mg/L.

E-waste Gold Refining - <i>Thiourea</i> Reduction - Metals in Solution (mg/L)											
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Leach	155064	1	5	2	0	28	29	4	15	1	13
Post Reduction Filtrate	1580	1	5	2	0	28	25	3	12	1	0

- [00557]** To further show the efficacy of *thiourea* as an Au specific reducing agent, Table 6E below shows the metals present in the partially aqueous refining solution post-leach, or dissolution of the gold, and in the post-reduction filtrate when dosed with *thiourea* and allowed to react. This reduction was also carried out in a hot water bath at 60°C. The *thiourea* was able to reduce over 99.5% of the Au in solution. In addition to this further improvement in the reduction, the remainder of the metal impurities in the solution remain untouched.

- 20 **[00558]** Table 6E: Summary of metals present in solution before and after gold reduction in the partially aqueous refining solution, using thiourea as a reducing agent (Thiourea 3), reduction carried out in a hot water bath. Numbers displayed in mg/L.

E-waste Gold Refining - <i>Thiourea</i> Reduction - Metals in Solution (mg/L)											
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Leach	161555	1	6	2	0	52	29	4	9	1	0
Post Reduction Filtrate	273	0	5	2	0	48	27	4	4	1	0

[00559] All the gold from the reducing experiments discussed above was subjected to a 1 M *thiourea* and 0.5 M *hydrochloric acid* aqueous rinse and dried and the purity of each sample was determined using digestion of the gold with reverse-aqua regia. The results of this analysis were used to calculate the purity of the gold using the following Equation 1:

5
$$Purity \% = \left(\frac{1,000,000 - SUM \left(Impurities \text{ in } \frac{mg}{kg} \right)}{1,000,000} \right) * 100\% \quad (1)$$

[00560] In Table 6F below, the results of those purity analyses of 4 of the 5 reductions discussed above are shown. Thiourea 2 (Table 6D) purity was not calculated, but based on the context and results of reductions shown here, it is expected that it would have also reached 99.99% purity. Each experiment resulted in 99.99%. However, the *thiourea* reductions clearly
10 show the lowest Ag left in the solid gold, and as this is a primary impurity of concern here, thiourea as reducing agent was considered most fit-for-purpose. The *sodium metabisulfite* and *sodium sulfite* reduced gold also required an extra step of a pre-rinse before the leach to get a 99.99% result.

15 [00561] Table 6F: Summary of key impurities found in gold solid after the refining method using various reducing agents, in milligrams per kilogram, carried out on e-waste gold.

E-waste Gold Refining - Impurities Present in Gold (mg/kg)											
Reducing Agent	Purity (%)	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Sodium Metabisulfite	99.99%	0	0	0	0	21	0	0	0	0	12
Sodium Sulfite	99.99%	0	0	0	3	7	1	3	0	0	0
Thiourea 1	99.99%	0	0	0	1	0	0	29	0	0	0
Thiourea 3	99.99%	0	0	5	0	4	6	7	0	0	17

[00562] Water Content

[00563] Section "Example 6 - Selected Examples of Chemical Processing - Water
20 Content" describes a variety of experiments that involve decreasing the glacial acetic acid content of the refining solution and increasing the water content to determine acceptable water levels, if any. As mentioned, only the Au leaching, or dissolving step was described, and thus only the leaching will be discussed here in the results. As noted above, in many cases little to

no gold was leached, and so those experiments were abandoned and not carried through to reduction and rinse steps.

[00564] Each initial experiment described was carried out in a way that would replace portions of the *glacial acetic acid* with *water* and left the portion of concentrated *HCl* and *NaClO₃ solution* as consistent as possible. The non-aqueous refining solution had a 5.5:1 phase ratio solution with 55% by volume *glacial acetic acid*, with no additional *water* added.

[00565] Below, Table 6G is a compilation of these experimental recipes, their corresponding phase ratios, and the gold leaching of each to directly compare the results.

10 [00566] Table 6G: A table summarizing results of experiments detailed in “Example 6 - Selected Examples of Chemical Processing - Water Content”. This table contains the refining solution for each experiment, the % of glacial acetic acid it contains, and how much gold was leached.

	Refining Solution Components Volume (mL)				<i>glacial acetic acid</i>	m _{Au} (g)	Phase Ratio	Sample Concentration (mg/L, ICP-OES)	Au Leached*
Exp.	Acetic Acid	HCl	Water	NaClO ₃	% by volume	Au	Solution :Au	Au	%
i	0.0	2.0	7.5	0.5	0%	1.0	10	6432	6%
ii	0.0	2.0	3.0	0.5	0%	1.0	5.5	105326	56%
iii	0.5	2.0	7.0	0.5	5%	1.0	10	1678	2%
iv	0.5	2.0	2.5	0.5	9%	1.0	5.5	135247	72%
v	2.0	2.0	5.5	0.5	20%	1.0	10	24440	24%
vi	1.0	2.0	2.0	0.5	18%	1.0	5.5	140540	78%
vii	1.8	2.0	1.5	0.8	30%	1.0	6.1	155633	94%
viii	3.0	4.4	1.6	1.0	30%	2.0	5	184329	92%

15 Note* that this is an estimated leach efficiency, as the high mg/L of Au in solution approaches or even exceeds the high end of the sensitivity of the standards used with the ICP-OES instrument. It is likely that the numbers over 100000 mg/L may be under reported by the ICP-OES. Thus, the estimated leach efficiency was calculated using Equation 2 below taking into consideration the amount of gold in solution and the initial gold brought into the leach.

20
$$Leach\ Efficiency = \left(\frac{concentration \left(\frac{mg}{L} \right) * volume\ of\ solution\ (L)}{initail\ mass\ Au} \right) \quad (2)$$

[00567] To otherwise quantify leach efficiency, best practice would include isolating the remaining gold, if any, and quantify it. This was not carried out for these experiments because they were investigative tests used to inform the development of the herein described refining methods.

- 5 [00568] As show in Table 6G, a 10:1 and ~ 5-6:1 phase ratio was tested. It was found that the lower phase ratio offered a relatively more effective leach and allowed for more gold leaching/dissolving. It was considered that this was due to an increased strength/concentration of the chemical components at this lower phase ratio.

- [00569] If only the ~5-6:1 phase ratio leach experiments are considered - ii, iv, vi, vii,
10 and vii - there was an observed increase in gold leaching as the amount of *glacial acetic acid* in the leach is increased, with the highest percentage of Au leached being at 30% by volume in solution. For experiment viii, there was some minimal visible gold was left over, but the outcome of this experiment was still considered successful when compared to experiment vii - which had a greater amount of oxidant added comparatively to the mass of gold in the leach,
15 and a smaller phase ratio.

[00570] **Dosing Regimes**

- [00571] With reference to Section "Example 6 - **Selected Examples of Chemical Processing** - Dosing Regimes", there were different dosing methods and regimes that were
20 considered. Below, results from experiments where continuous dosing with a dosing pump was carried out is compared to two experiments in which manual dosing was used - one with 3 doses every 3 minutes and one with 3 doses every 1 minute. For ease of comparing mg/L in solution for each experiment, each described experiment was carried out at a 5.5:1 phase ratio with 55% *glacial acetic acid* by volume recipe.

- 25 [00572] Table 6H below contains the metals present in the refining solution post-leaching for 3 leaches, each with a different timing of oxidant dosing. The first leach was conducted at a 10 g scale using a dosing syringe pump that delivered 1 mL/min for 5 minutes. The second leach was conducted at a 10 g scale using manually dosing with a pipette, dosing 1.66 mL at 0, 3 and 6 minutes. The third leach was conducted at a 20 g scale using manual
30 dosing with a pipette, dosing 3.34 mL at 0, 1 and 2 minutes.

[00573] In the context of this dosing study, metals other than Au presented in Table 6H varied because the source gold for each experiment was different and impurities present will and do vary. Something to note when considering these results is, as mentioned before, the

high mg/L of Au in solution approaches or even exceeds the high end of the sensitivity of the standards used with the ICP-OES instrument. It is likely that the numbers over 100000 mg/L may be under reported by the ICP-OES. If these numbers were taken and used to calculate how much gold was present in solution, it would be lower than the input gold. However, each reaction saw no visible gold left over, and the resultant leached mixture was bright orange as expected. Taking this into account and looking at the gold values in the table for each leach, they are within approximately 2.5% of each other. This number variance may be attributed to the purity of the input gold varying, or due to sampling, and it was considered reasonable to conclude that the leaches performed similarly across the different oxidant dosing methods and timings.

[00574] Table 6H: A table summarizing metals in solution for three different refining leaches, with different oxidant dosing regimes. Metals in solution presented in mg/L.

Sample	Concentration of metals in solution (mg/L)									
	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni
Dosing Pump - 5 minutes	158631	4	11	9	1	24	683	11	117	13
Discrete dosing - 6 min	154067	1	2	57	226	49	20	51	21	0
Discrete dosing - 2 min	156197	0	4	53	219	15	17	42	15	2

[00575] Thus, it was considered that any of these dosing regimes could be applied For experiments described herein, manual dosing over 2 minutes was selected for lab scale experiments, and continuous pump dosing over 5 minutes was selected for large scale experiments (for example, when using the system as described herein)is used.

[00576] Rinses

[00577] With reference to section "Example 6 - **Selected Examples of Chemical Processing - Rinses**" six rinse variations are described. Below, the ICP-OES analysis of these rinses is presented in three different tables. The results are presented in separate tables because each of the three sets was carried out on different sets of gold, and so the rinses are only compared to ones in its set. However, in this discussion, the whole set was considered when determining to use 1M thiourea and 0.5M HCl rinse for the experiments described herein.

[00578] Table 6I below shows the comparison of 3M *HCl* and 3M *HNO₃* rinses, both carried out for 30 minutes at 50°C. Neither of the rinses presented could remove Ag impurities present in the gold powder at these conditions. Although the 3M *HNO₃* rinse could remove approximately ten times the Pb, Cu, Fe and Ni impurities from the gold, it was decided that *HNO₃* would be avoided as a rinsing agent in case any *HCl* remained left over after the leaching and reduction process. If any *HCl* remained, there would be the possibility of the production of *NO_x*, a brown gas that is the byproduct of the reaction of *HCl* and *HNO₃* in aqua regia and is very toxic.

10 **[00579]** Table 6I: A table summarizing impurities removed from powdered gold when subjected to a 3M *HCl* or 3M *HNO₃* rinse for 30 minutes at 50°C. Metals in solution presented in mg/L.

	Concentration of metals in solution (mg/L)									
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni
3M <i>HCl</i> Rinse	0	-	0	1	26	0	36	49	0	2
3M <i>HNO₃</i> Rinse	195	-	0	1	231	0	328	479	1	22

15 **[00580]** The next set of rinses compared is 0.5M *HCl* and 1M *thiourea*, both carried out at room temperature for 10 minutes. Table 6J below shows impurities removed from the gold powder in each rinse. The *HCl* rinse was effective at removing Sn, Pb, and Fe impurities from the gold while the *thiourea* rinse removed a relatively large amount of Ag from the gold powder. Neither rinse on its removed the whole spectrum of impurities of concern, but this experiment a combination of these two rinses together could remove more of the impurities.

20

[00581] Table 6J: A table summarizing impurities removed from powdered gold when subjected to a 0.5M *HCl* or 1M *thiourea* rinse at room temperature for 10 minutes. Metals in solution presented in mg/L.

	Concentration of metals in solution (mg/L)									
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni
<i>HCl</i> Rinse	1	0	0	32	137	1	4	23	2	0
Thiourea Rinse	118	0	0	0	2	26	0	1	0	0

[00582] Table 6K below shows a comparison of a 1M thiourea and 0.5 M HCl rinse to a 1.5 M sodium thiosulfate rinse. The combination of the thiourea and HCl rinse did remove a wider spectrum of impurities of concern in gold powder. When compared to the sodium thiosulfate rinse, the thiourea and HCl rinse could remove a relatively greater amount of Sn, Pb, Ag and Fe impurities. It was also noted that - in the presence of an acid - sodium thiosulfate decomposes into SO₂ gas, and elemental sulfur precipitates, leaving behind a cloudy yellow solution. Thus, like in regard to forming NO_x, if any acid was not properly rinsed away from the gold powder after the leaching and precipitation process, there is a chance that this precipitate could form and interfere with the rinsing process.

[00583] Table 6K: A table summarizing impurities from powdered gold when subjected to a 0.5M HCl and 1M thiourea or 1.5M sodium thiosulfate rinse at room temperature for 10 or 30 minutes respectively. Metals in solution presented in mg/L.

Sample	Concentration of metals in solution (mg/L)									
	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni
Thiourea & HCl Rinse	222	0	0	37	239	49	7	36	2	1
Sodium Thiosulfate Rinse	499	0	1	4	130	2	10	3	7	1

[00584] Temperature Testing

[00585] It was noted that, when reducing gold - for example, with thiourea - an intermediate gold complex may form that is white in colour and very bulky. Although the reduction reaction itself is exothermic, it may not provide enough heat for the gold to completely react to its metallic form. The series of experiments described in Section "Example 6 - **Selected Examples of Chemical Processing** - Temperature Testing" were investigate a method to speed up this reaction and convert the gold from this intermediate bulky white complex to metallic gold powder.

[00586] The experiments, as presented in Table 6L, were carried out using the 55% *glacial acetic acid* refining solution. Table 6L below shows the gold in solution after 120 minutes of reaction time in each of the vials. the results of the ice bath reduction suggested that heat supports reduction. Although the remaining numbers look relatively comparable, it was observed that the room temperature and 45°C reductions showed evidence of the white bulky intermediate up until the last sample at 120 minutes, and this intermediate was not present in

the 60°C sample even in the 20-minute sample. It was also noted that the ice bath reduction sample had notably high amounts of the intermediate through the whole reduction.

- [00587] Table 6L: A table summarizing metals left in solution following 120 minutes of a thiourea reduction of gold at room temperature, 60°C hot water bath, 45°C hot water bath or an ice bath. The numbers are presented in the context of the refining solution post-leach to be able to compare how much gold has been reduced. Metals in solution presented in mg/L.

	E-waste Gold Refining - Thiourea Reduction - Metals in Solution (mg/L)										
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Leach	154013	1	8	3	1	14	59	8	16	2	1
RT Reduction	3951	1	8	3	0	5	51	6	11	2	0
60°C Reduction	5435	1	8	3	0	14	50	6	12	2	0
45°C Reduction	4870	1	8	3	0	12	51	6	14	2	0
Ice Bath Reduction	24310	1	8	3	3	10	51	7	11	2	2

- [00588] Figure 3 shows the progression of the gold reduction in photos at 20, 40, 60 and 120 minutes of reaction, in the order (left to right) that the values in Table 6L are presented for room temperature, 60°C, 45°C, and ice bath. The bulky intermediate gold complex can also be seen in these images, particularly for the reduction carried out in the ice bath, depicted on the far right of each photo.

- [00589] Using the numerical results and the qualitative visual results of the reduction, 60°C was identified as a suitable temperature to carry out gold reduction. At this temperature, it was possible to bypass the bulky intermediate solid before any sampling was done, to reduce, minimize, or prevent gold being lost to this complex. Avoiding this loss is important, as recovering gold while it is in this complex includes re-leaching or collecting it in aqua regia, extending and complicating the process.

- [00590] In view of the results presented above, a quadruplicate test was carried out to determine whether the gold reduction at 60°C was reproducible. First the quadruplicate was carried out with the 55% *glacial acetic acid* by volume refining solution. As presented in Table 6M below, the values were consistent across the 4 samples. The amount of gold left in solution was lower than in the initial trial, and perhaps this may be attributed to the fact that these samples were only removed from the hot water bath and centrifuged to sample twice, whereas

the initial trial included 4 centrifuging and sample steps, and may interrupt the reduction process.

- [00591]** Table 6M: : A table summarizing metals left in solution after a gold reduction of a 55% glacial acetic acid by volume gold leach recipe, using thiourea as a reducing agent and carried out in a hot water bath at 60°C. A quadruplicate experiment was carried out to ensure reproducibility. Metals in solution presented in mg/L.

	E-waste Gold Refining - <i>Thiourea</i> Reduction - Metals in Solution (mg/L)										
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Leach	155064	1	5	2	0	28	29	4	15	1	13
Reduction 1	1580	1	5	2	0	28	25	3	12	1	0
Reduction 2	1662	1	5	2	0	27	24	3	6	1	2
Reduction 3	1944	1	5	2	0	26	24	4	7	2	1
Reduction 4	1710	1	5	2	0	27	25	3	7	1	0

- [00592]** Another quadruplicate test was carried out to test reproducibility of gold reduction at 60°C. This quadruplicate was carried out with the 30% *glacial acetic acid* by volume refining solution. As presented in Table 6N below, the values were consistent across the 4 samples. These numbers were lower than those in the 55% recipe, so this combination of *thiourea* reduction at 60°C was demonstrated to be relatively more effective.

- [00593]** Table 6N: A table summarizing metals left in solution after a gold reduction of a 30% glacial acetic acid by volume gold leach recipe, using thiourea as a reducing agent and carried out in a hot water bath at 60°C. A quadruplicate experiment was carried out to ensure reproducibility. Metals in solution presented in mg/L.

	E-waste Gold Refining - <i>Thiourea</i> Reduction - Metals in Solution (mg/L)										
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Leach	161555	1	6	2	0	52	29	4	9	1	0
Reduction 1	415	1	5	2	0	49	26	3	5	1	0
Reduction 2	273	0	5	2	0	48	27	4	4	1	0
Reduction 3	303	0	5	2	0	47	25	4	5	1	0
Reduction 4	569	0	5	2	0	47	26	4	2	1	0

[00594] Scale Up – Refining System As Described herein

- [00595]** In one or more examples of the refining system described herein, the system has a small spatial footprint with the capability of processing 1 kg of gold per day. As the

refining methods described herein at lab scale could take approximately 2 hours from beginning to end, it was considered that a larger scale refining system could manage 2 runs per day with a 500 g input of gold to reach 1 kg.

[00596] The experiment outlined in "Example 6 - **Selected Examples of Chemical Processing - Scale Up**", from beginning to end, counting all pumping time, took 3 hours and 38 minutes. (The saturated *thiourea* solution preparation was not counted as part of this time frame, this solution could be made up in advance (for example, approximately once a week) to keep up with reducing and/or rinsing needs.

[00597] While the Scale-Up experiment was carried out on a scale of 420 g out of the possible 500 g, it is still expected that 2 runs of 500 g could be carried out per day provided extra time should be accounted for to pump and filter the slightly larger volume.

[00598] Table 6O below shows a summary of the metals in solution at the various sampling steps in the refining method. The discrepancy between the post-reduction gold number in the top sample and the filtrate may be attributed to the first sample being taken off of the top and likely containing lightweight gold fines that were not centrifuged in the sample preparation step. After the filtration, the filtrate has been pumped through the filter twice - once to be kidney looped back into the reactor, and another time through a polishing filter to the filtrate solution container - so any remaining fines may be captured, and the number 210 mg/L represents the actual gold left in solution that is not reduced by the thiourea solution.

[00599] Table 6O: A table summarizing metals in solution in the leach, post reduction filtrate, and the thiourea/HCl rinse of a 420 g run through the scale up refining reactor. Metals in solution provided in mg/L.

	E-waste Gold Refining - Metals in Solution (mg/L)										
Sample	Au	Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Leach	162397	0	1	1	0	7	13	0	2	0	1
Post Reduction - Top Sample	2045	0	3	2	2	37	92	18	9	4	1
Post Reduction Filtrate	210	1	4	3	2	40	96	21	65	5	11
Thiourea/HCl Rinse	137	0	0	0	0	2	2	0	4	0	0

[00600] It was noted that - in both Post Reduction Filtrate samples - there is more Ag in solution than in the original Leach solution. Without wishing to be bound by theory, it was considered that the reason for this may be as follows: The filters in place between the Leach

and the Reduction reactor are used run over run. For the purposes of commissioning, after each run, the system is flushed with water to collect any locked-up gold containing solution (that is, leached solution) - and then the cartridge filters are removed from the system, dried, weighed and photographed to document how the filters are affected over time. Some leached solution may remain, and once the filters are installed for the next run, anything left over could be carried over by the new refining solution/leached solution to the reduction reactor. So, if the input gold of one run has more Ag impurities, they may be carried over. Either way, this carry over was not considered a concern, because - as displayed below in Table 6P - there was no Ag in the final gold that was collected from the refining system. Additionally, this refining system may be run back-to-back, day over day, without flushing the system in between each run, with the consideration that any gold locked up in the system may be collected with the next leach and reduction procedure.

[00601] Additionally, it was observed that - in the *thiourea* and *HCl* rinse - there was 137 mg/L Au. This may again be attributed to sampling from the top, and gold fines not being centrifuged in the sample preparation step. This rinse was not sampled at later steps because it was collected in an aqueous waste container that was used run over run.

[00602] Table 6P: A table summarizing metallic impurities remaining in powdered gold after a refining cycle through the scale up refining reactor. Metal impurities in solid gold presented in mg/kg.

Sample	Purity (%)	E-waste Gold Refining - Impurities Present in Gold (mg/kg)									
		Pt	Pd	Sn	Pb	Ag	Cu	Fe	Zn	Ni	Al
Refined (In-house Analysis)	99.998%	0.0	0.0	12.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[00603] Table 16 above shows that the only impurity of note remaining in the gold powder after the refining process was Sn, and this thus equates to a purity of 99.998%.

[00604] **Example 7 - A System for Refining a Precious Metal**

[00605] The example that follows discusses a system in the context of refining gold; however the system may also be used in the refining of other precious metals.

[00606] **System Operation**

[00607] In an embodiment of the present disclosure, the system as described herein and as depicted in Figure 1 may be operated as follows. Refining solution may be referred to here as leach solution or leach mixture. Leached solution to which reductant is added may be referred to here as a reduction solution.

5 [00608] **Gold Leach**

[00609] This following lists steps to leach gold using the system as described herein. Steps mostly occur within the Leach Reactor 1.

Prepare for leach dosing of Chemical Pump 2-R1 (solvent), Chemical Pump 2-R2 (acid) and Chemical Pump 2-R3 (oxidant).
Collect feedstock (unrefined gold powder <250 um particle size). The feedstock remained stored in a sealed container until it is added to the Leach Reactor 1.
Press "START" button on Chemical Pump 2-R1 (solvent). Wait for the pump to complete dosing. Monitor the lines for blockages or other issues.
Press "START" button on Chemical Pump 2-R2 (acid). Wait for the pump to complete dosing. Monitor the lines for blockages or other issues.
Press the "START" button on Leach Reactor Agitator 13 (See Figure 1).
Open a Gold Powder port (see Figure 1, Solid Au) on the lid of the Leach Reactor 1. Carefully transfer the gold powder into Leach Reactor 1. Close the Gold Powder port on the lid of the Leach Reactor 1.
Press the "START" button on Chemical Pump 2-R3 (oxidant). Start a leach reaction timer. Chemical R3 (oxidant) dosing will occur over part or all of the duration of the leach reaction. Continuously monitor the lines for blockages or other issues. Allow the leach reaction to proceed to conclusion. Generally 10-20 minutes, or until a visual indication that feedstock has all been leached.

Press the "STOP" button on the Leach Reactor Agitator 13. Press the "START" button on the Reduction Reactor Agitator 14(see Figure 1) in the Reduction Fume Hood. Allow the leached solution and suspended solids to drain from the Leach Reactor 1 via first polishing system comprising pump 4 and Leach Filter 3*, and for the leached solution to transfer to the Reduction Reactor 6. Monitor the transfer lines, pump, and filter for blockages or other issues. Wait for the transfer to complete.
Set the Reduction Reactor 6 heating jacket switch to "HEAT ON" (not shown in Figure 1).
Prepare for the post-leach displacement flush of Chemical Pump 2-R1 (solvent). Press the "START" button on Chemical Pump 2-R1. Wait for the pump to complete dosing. Monitor the lines for blockages or other issues. Turn on Leach Transfer Pump 4. Allow the displacement flush to drain from the Leach Reactor 1, pump through the Leach Filter 3*, and transfer to the Reduction Reactor 6.

[00610] Gold Reduction

[00611] The following lists steps to precipitate solid high purity gold powder out of the leached solution from the previous section. Steps mostly occur in the Reduction Reactor 6.

Prepare for reduction dosing of Chemical Pump 10 (reductant)
Press the "START" button on Chemical Pump 10 (reductant). Wait for the pump to complete dosing. Monitor the lines for blockages or other issues. Start the reduction reaction timer.
Turn on Reduction Transfer Pump 7 (see Figure 1) to "ON". Press the "STOP" button on the Reduction Reactor Agitator 14 .

If conducting post-reduction kidney loop filtering via second polishing filter system:

- 1.1 Start recirculation timer.
- 1.2 Allow reduction solution to recirculate through the reduction reactor and second polishing filter system. Continue for as long as needed.
- 1.3 During kidney loop, agitation is kept to further facilitate reducing gold. After kidney looping, agitation is stopped for filtration.

Else-If:

- 1.4 Continue.
- 1.5 Allow reduction solution to filter through the filter system in the bottom of the Reduction Reactor, pump through the Trace Gold Solution Filter 11, and drain into the Trace Gold Solution Holding Tank, otherwise referred to as a spent solution storage tank.
- 1.6 Monitor the transfer lines, pump, and filter to blockages or other issues.
- 1.7 Wait for the transfer to complete.

Prepare for post-reduction displacement flush of Chemical Pump 5-R4 (aqueous/water).

Press "START" button on Chemical Pump 5-R4.

Wait for the pump to complete dosing.

Turn on Reduction Transfer Pump 7.

Allow the Chemical R4 (aqueous/water) to pump through into the Trace Gold Solution Holding Tank. This will displace residual trace gold solution remaining in the lines/fittings/pump/etc. Initial water rinse goes through Filter 12 to be sent to aqueous waste storage.

[00612] Gold Rinse

[00613] The following lists steps to rinse residual impurities from the solid high purity gold powder precipitated in the previous section.

5 **[00614]** The rinsing may include:

- One or more rinse cycles
- Single or multi-reagent rinses (one or more of Chemical R2 (acid), Chemical R6 (reductant) and/or Chemical R4 (aqueous solution, water) for a given rinse)
- Recirculation or no recirculation of rinse solution

For each chemical R2, R4, R6:
1.8 Set pumping parameters.
1.9 Press "START" button on the respective chemical pump.
1.10 Wait for the pump to complete dosing. Monitor the lines for blockages or other issues.
Start the rinse timer.
Set the Reduction Reactor Agitator 14 .
Press "START" button on the Reduction Reactor Agitator 14.
Wait for the rinse duration.
Press "STOP" button on the Reduction Reactor Agitator 14.
Turn on Reduction Transfer Pump 7.
If conducting recirculation for rinse filtering via second polishing filter system:
1.11 Start recirculation timer.
1.12 Allow rinse solution to recirculate through the reduction reactor. Continue for as long as needed.
Else-If:
Continue.
Allow the rinse solution to filter through the filter system in the bottom of the Reduction Reactor 6, pump through the Aqueous Waste Filter 12, and drain into the Aqueous Waste Holding Tank (see Figure 1).
Monitor the transfer lines, pump, and filter to blockages or other issues.
Wait for the transfer to complete.
Repeat this section for additional rinses, as needed.

[00615] Gold Removal

[00616] The following lists the steps required to disassemble the Reduction Reactor to remove the filter medium and solid high purity gold powder.

Place a clean container under the Reduction Reactor 6.
Carefully remove the filter system from the Reduction Reactor base. Place it in the container. Carefully remove gold on the inside of the upper portion of Reduction Reactor 6, impeller and impeller shaft into the container.

[00617] Reducing Mixture Preparation

[00618] The following lists steps for preparing the reducing mixture. Reductant used in the reducing mixture is not provided in its liquid form and so the reducing mixture is prepared from a combination of water/aqueous solution and solid reductant powder. For example, the preparing the reducing mixture may involve adding about 50% of the water (R4) into the reagent make-up reactor 9, then dose reductant into reactor 9, and then flush dosing funnel (not shown in Figure 1) with remaining water to clean out any residual reductant. Aqueous reductant solution may be prepared for up to a week's worth of use.

Turn on Reactor 9 heating jacket to temperature of 30°C
Pump R4 into Reactor 9
Start Agitator 15 of Reactor 9
Dose solid reagent R5 (oxidant) into Reactor 9 using solids dosing system.
Keep agitation on for 60 minutes or until the reagent fully dissolves.
End the Heating. When the reaction is complete turn off the heater.

[00619] Chemical Dosing Setup

[00620] The following describes steps for accurate chemical dosing of Chemicals R1 (solvent), R2 (acid), R3 (oxidant), R5 (reductant); R6 (reducing mixture); and R4 (water/aqueous solutions). This includes line priming, and dosing pump configuration.

i. Accurate dosing of chemicals into the target reactor relies on the lines (tubing, fittings, pumps, etc.) being filled with liquid. If the lines are not primed, doses delivered to the target reactor could be below expected volume.

ii. Configure the reagent pumps for dosing volumes required. Some reagent pumps may need to be reconfigured for alternate dosing volumes depending on stage of the process and if one dosing pump is used for multiple reactors (see note on Fig. 1).

iii. During rinse stages of reduction/precipitation, transfer pump 10 and dosing reagent pumps 5 will be reconfigured at each rinse stage as they are used several times.

iv. If dosing reagent pumps 2 and 5 are the same servicing pump for R2, then it will need to be re-configured during the gold rinse stage.

5

- v. Dosing reagent pump 2 for reagent R2 will need to be re-configured between the gold leach and reduction stages.
- vi. If dosing reagent pumps 5 and 8 are the same servicing pump for R4, then it will need to be re-configured between the reductant make up stage and the rinse stages.

[00621] **Filter System**

[00622] The following lists steps for installing the filter system 20 in Reduction Reactor 6 and test that the bottom of the reactor is liquid tight before operating.

This procedure assumes that the filter system is already disassembled from the upper portion of Reduction Reactor 6. Confirm that all parts of the filter system are available: 1.13 Centering ring 21 1.14 Filter medium 22 1.15 Perforated plate 23 1.16 Filter base 24 1.17 Filter base O-ring (not pictured in Figure 2) Inspect the filter base system: 1.18 No residual gold on surfaces 1.19 No cracks or damage to the centering ring, perforated plate, or filter base 1.20 No excessive wear/damage to the filter base O-ring that would prevent it from properly sealing
1.21 Place the filter medium 22 on top the perforated plate 23. Note: Some filter mediums may have one side with a smooth surface texture. Install the medium with that side facing upwards.
Ensure that the filter base O-ring is fully seated in the groove on the top of the filter base 24.
Fix the centering ring 21 on top of the filter medium 22 and make sure it is pushed down on all edges evenly. Line up the filter base 24 assembly with the reactor 6 and place the vessel clamp and tighten the torque knobs until it clicks. Do not overtighten the vessel clamp.

Fix the centering ring 21 on top of the filter medium 22 (for example, frit) and make sure it is pushed down on all edges evenly. Line up the filter base 24 assembly with the reactor 6 and place the vessel clamp and tighten the torque knobs until it clicks. Do not overtighten the vessel clamp.
Configure Chemical R4 Pump to fill the Reduction Reactor 6 according to the volume needed. Press the "START" button on the Chemical R4 Pump. Wait for the dosing to complete. Run a timer to confirm proper seal hold based on the duration needed. Wait for completion. Visually inspect the Reduction Reactor 6 for leaks, shifting of filter media, etc.
Allow the reagent R4 to filter through the filter system 20 in the bottom of the Reduction Reactor 6, pump through the Aqueous Waste Filter 12, and drain into the Aqueous Waste Holding Storage Tank.
If the visual inspection of the Reduction Reactor 6 for leaks, shifting of filter media, etc. identified no deficiencies: 1.22 End this auxiliary procedure. Return to primary procedure. Else-If: 1.23 Repeat this auxiliary procedure until correct setup can be confirmed.

[00623] Filtration Testing Of Filter Medium 22 – Lab scale

[00624] The objectives of this test were to (1) assess the filterability of the process fluid/slurry (for example, spent leached solution and precipitated precious metal) and (2) characterize the resulting cake, to enable a recommendation for the type and size of filter medium (frit, filter paper, etc.) best suited for the process under vacuum.

[00625] Three tests were performed with a pre-filtration of the Pregnant Leached solution to remove solid impurities, using a 3-micron depth filter. For all leach filtration, the cartridge was installed upside down to minimize solution lockup and a peristaltic pump was used to pump solution through the filter. The volume of the leached solution was at 313 ml for three repeats. The leached filtration was successful and took ~10min. For all repeats, the 3-micron filter successfully filtered out solids. Note that the filter cartridge was not flushed in between tests to ensure filter robustness over several runs.

[00626] Next, a reduction step was performed to precipitate refined gold out of solution and the resulting slurry was vacuum filtered through a Nutsche Filter and rinsed. The results were analyzed and showed good cake buildup and filterability of the slurry. The experimental data of the reduction filtration is summarized below. Note that for cake thickness measurements, the lowest cake height was measured.

[00627] **Filtration Tests - Refining Reduction 1**

[00628] Setup

[00629] Nutsche filter with vacuum pump

[00630] 5 micron PP (McMaster) (0.45mm thick)

10 [00631] Paper weight (g) 0.321

Reduction Solution		Gold Cake	
Pressure (mmHg)	-175	Wet (g)	55.979
Time (s)	Reduction Volume (mL)	Dry (g)	54.2828
0	0	Moisture Content	3.1%
5	200		
18	323	** no thickness measurements	

** Gold observed in the reduction filtrate

R4 Rinse 1		R6 Rinse	
Pressure (mmHg)	0	Pressure (mmHg)	-200
Time (s)	Rinse 1 Volume (mL)	Time (s)	R6 Rinse Volume (mL)
0	0	0	0
22	50	10	70
47	70	15	100
72	100	23	150
125	150	30	200
191	200	36	250
291	250	45	275
501	300	70	288
659	350		
874	400		
1026	430		

R4 Rinse 2	
Pressure (mmHg)	-200
Time (s)	Volume (mL)
0	0
12	200
132	210

[00632] Filtration Tests - Refining Reduction 2

[00633] Setup

[00634] Nutsche filter with vacuum pump

5 **[00635]** 5 micron PP (McMasterr) (0.44mm thick)

[00636] 2 micron paper (USALAB) - 0.13 mm

Gold Cake	
Wet (g)	54.751
Dry (g)	53.1698
Moisture Content	3.0%
Gold thickness (mm)	8.12

Reduction Solution	
Pressure (mmHg)	-550
Time (s)	Volume (mL)
0	0
13	50
19	70
25	100
39	150
53	200
70	250
87	300
109	345
**no gold fines in the reduction filtrate	

R4 Rinse 1	
Pressure (mmHg)	-450
Time (s)	Volume (mL)
0	0
11	50
19	70
32	100
74	150
215	178

R6 Rinse	
Pressure (mmHg)	-550
Time (s)	Volume (mL)
0	0
10	50
14	70
20	100
26	150
34	200
47	250
58	288

R4 Rinse 2	
Pressure (mmHg)	-500
Time (s)	Volume (mL)
0	0
29	50
41	70
52	100
84	122
** 2 min dry time after	

[00637] Filtration Tests - Refining Reduction 3

[00638] Setup

[00639] Nutsche filter with vacuum pump

5 **[00640]** 5 micron PP (McMasterr) (0.44mm thick)

[00641] 2 micron paper (USALAB) - 0.13 mm

Gold Cake	
Wet (g)	57.2648
Dry (g)	54.989
Moisture Content	4.1%
Gold thickness (mm)	9.64

Refining Reduction	
Pressure (mmHg)	-575
Time (s)	Volume (mL)
0	0
23	50
32	70
45	100
75	150
99	200
131	250
173	292

R4 Rinse 1	
Pressure (mmHg)	-550
Time (s)	Volume (mL)
0	0
21	50
39	70
69	100
117	142

R6 Rinse	
Pressure (mmHg)	-575
Time (s)	Volume (mL)
0	0
10	50
15	70
22	100
34	150
47	200
59	250
73	280

<i>R4 Rinse 2</i>	
Pressure (mmHg)	-500
Time (s)	Volume (mL)
0	0
11	50
17	70
26	100
44	150
59	195

[00642] Filtration – Adaptations

[00643] Filtration tests delineated below were undertake on the system was described here, an example of which is presented in Figure 1.

5 **[00644] FRA 01: Filter Reactor Commissioning**

[00645] Experiment parameters:

[00646] 235g of unrefined gold was leached in lab and the leach was filtered using a buchner funnel in lab. Then, the filtered leach solution was transferred into the reduction reactor to begin reducing gold.

10 **[00647]** Reduction Filtration setup was as follows:

- Filter reactor with 2micron USALAB paper + 5micron PTFE frit
- No Kidney looping (also referred to herein as second polishing filter system) of filtrate
- Spent solution went through a cartridge filter (3 micron)
- Rinse solution went through a cartridge filter (3 micron)

15 **[00648] Result:**

[00649] Reduction spent solution:

- Four min filtration for 1,500ml of Reduction solution (flowrate of 375ml/min)

[00650] Rinse filtrations:

- R4 rinse 1: 3 min filtration for 1410ml (flowrate of 470 ml/min)
- 20 - R4/R6/R2 rinse 2: 3 min filtration for 1174ml (flowrate of 391 ml/min)
- R4 rinse 3: 3.4 min filtration for 1410ml (flowrate of 415 ml/min)

[00651] Observations:

[00652] Due to a filter reactor setup where the filter medium was exposed to the reduction reaction of 60 minutes and more, the USALAB 2-micron paper disintegrated, and the
25 solution filtered through the 5-micron PTFE frit only. For next experiment, PTFE and

polypropylene filter papers were used instead as it was considered that they would be relatively more robust filters. Some solution passed through the frit during reduction reaction that still contained gold.

- 5 [00653] **FRA 02: 60% chemical commissioning**
- [00654] **Experiment parameters:**
- [00655] 420g of unrefined gold was leached and reduced in respective reactors 1 and 6.
- [00656] Leach Filtration setup was as follows:
- 10 - Leach solution filtered through a cartridge filter (3 micron)
- [00657] Reduction Filtration setup was as follows:
- Filter system was fitted with 5-micron PTFE frit
 - No Kidney looping of filtrate
 - Spent solution went through a cartridge filter (3 micron)
- 15 - Rinse solution went through a cartridge filter (3 micron)
- [00658] **Result:**
- [00659] Leach Filtration:
- Time not taken
 - Leftover feed due to poor agitation in leach reactor
- 20 - Filtration began when solution temperature was 42.1°C
- [00660] Reduction spent solution:
- 3.73 min filtration for 2,814ml of Reduction solution (flowrate of 754ml/min)
 - Filtration began when solution temperature was 63.8°C
- [00661] Rinse filtrations:
- 25 - R4 rinse 1: 2.2 min filtration for 2100ml (flowrate of 955 ml/min)
- R4/R6/R2 rinse 2: 2.75 min filtration for 2100ml (flowrate of 764 ml/min)
 - R4 rinse 3: 3.28 min filtration for 2100ml (flowrate of 640 ml/min)
- [00662] Cake Thickness: Average cake thickness from 3 measurements was 11.05mm
- [00663] Particle size analysis (PSA) on gold:
- 30 - D_{80} = 418.6 micron
- Range: 52.33 to 1408 micron
- [00664] **Observations:**

- [00665] Filtration with the 5micron PTFE frit was fast, however 0.42g of refined gold was captured in the pores of the filter. Hence, to minimize gold losses in the filter and extend the life of the PTFE frit, a disposable filter media was placed on top of the frit. Some solution passed through the frit during reduction reaction that still contained gold. The spent solution storage tank had visual gold precipitated, thus kidney loop step was added to the next run to minimize gold concentration of the spent solution (that is, leached solution from which the reduced precious metal was precipitated and separated). 10 minutes was chosen to give enough time for the reduction of gold in the solution that had bypassed the frit.
- 10 [00666] **FRA 03: 60% chemical commissioning**
- [00667] **Experiment parameters:**
- [00668] 420g of unrefined gold was leached and reduced in respective reactors 1 and 6.
- [00669] Leach Filtration setup was as follows:
- 15 - Leach solution filtered through a cartridge filter (3 micron)
- [00670] Reduction Filtration setup was as follows:
- Filter reactor with 0.45-micron PTFE, 0.45-micron PP, and 5-micron PTFE frit (order is from top to bottom)
 - These papers were selected as it allowed robustness against reaction, fast
 - 20 filtration time, and minimal solution break through during reaction.
 - Kidney looping of filtrate for 10 min
 - Only the reduction reactor filter was used in this step. The solution did not touch filter 11 (see Figure 1).
 - Spent solution went through a cartridge filter (3 micron)
 - 25 - Rinse solution went through a cartridge filter (3 micron)
- [00671] **Result:**
- [00672] Leach Filtration:
- 27 min filtration for 2100ml of leach solution (flowrate of 78 ml/min)
 - Complete leaching of feed due to agitation design
 - 30 - Filtration began when solution temperature was 44.9°C
- [00673] Reduction spent solution:
- 4.3 min filtration for 2,964ml of Reduction solution (flowrate of 689ml/min)

- Filtration began when solution temperature was 56.1°C
- [00674] Rinse filtrations:
- R4 rinse 1: 3.5 min filtration for 2100ml (flowrate of 600 ml/min)
 - R4/R6/R2 rinse 2: 2.4 min filtration for 2100ml (flowrate of 875 ml/min)
- 5 - R4 rinse 3: 2.8 min filtration for 2100ml (flowrate of 750 ml/min)
- [00675] Particle size analysis (PSA) on gold:
- D_{80} = 269.7 micron
 - Range: 15.56 to 592 micron
- [00676] Observations:
- 10 [00677] Filtration time with the finer papers stacked on top of the 5micron frit was comparable to FRA02 filtration times. Kidney looping minimized spent solution gold concentration to 210 ppm. Leach filtration was slow with the 3 micron cartridge filter. Ordered a 10" cartridge filter with higher surface area to improve filtration time.
- 15 [00678] **FRA 04: 3rd Party Gold**
- [00679] Experiment parameters:
- [00680] 200g of unrefined gold from 3rd party was leached and reduced in respective reactors 1 and 6.
- [00681] Leach Filtration setup was as follows:
- 20 - Leach solution filtered through 1301 cartridge filter (10" cartridge filter, 1 micron)
- [00682] Reduction Filtration setup was as follows:
- Filter reactor with 0.45-micron PTFE, 0.45-micron PP, and 5-micron PTFE frit (order is from top to bottom)
 - Kidney looping of filtrate for 10 min
- 25 - Only the reduction reactor filter was used in this step. The solution did not touch filter 11.
- Spent solution went through a cartridge filter (3 micron)
 - Rinse solution went through a cartridge filter (3 micron)
- [00683] Result:
- 30 [00684] Leach Filtration:
- 0.45 min filtration for 1020ml of leach solution (flowrate of 2267 ml/min)
 - Filtration began when solution temperature was 40.9°C

- [00685] Reduction spent solution:
- 1.9 min filtration for 1562ml of Reduction solution (flowrate of 822ml/min)
 - Filtration began when solution temperature was 50°C
- [00686] Rinse filtrations:
- 5
 - R4 rinse 1: 1.2 min filtration for 1000ml (flowrate of 833 ml/min)
 - R4/R6/R2 rinse 2: 1.3 min filtration for 1000ml (flowrate of 769 ml/min)
 - R4 rinse 3: 1.6 min filtration for 1000ml (flowrate of 625 ml/min)
- [00687] Cake Thickness: Average cake thickness from 5 measurements was 9.69mm
- [00688] **Observations/Learnings:**
- 10 [00689] Faster leach filtration with 10" housing cartridge filter (for example, see filter 3* of Figure 1).
- [00690] **FRA 05: 3rd Party Gold**
- [00691] **Experiment parameters:**
- 15 [00692] 440g of unrefined gold from 3rd party was leached and reduced in respective reactors 1 and 6.
- [00693] Leach Filtration setup was as follows:
- Leach solution filtered through a cartridge filter (10" cartridge filter, 1 micron) and a polishing cartridge filter (3-micron cartridge filter)
- 20 [00694] Reduction Filtration setup was as follows:
- Filter reactor with 0.45-micron PTFE, 0.45-micron PP, and 5-micron PTFE frit (order is from top to bottom)
 - Kidney looping of filtrate for 10 min
 - Only the reduction reactor filter was used in this step. The solution did not touch
- 25 filter 11.
- Spent solution went through a cartridge filter (3 micron)
 - Rinse solution went through a cartridge filter (3 micron)
- [00695] **Result:**
- [00696] Leach Filtration:
- 30
 - 2.1 min filtration for 2200ml of leach solution (flowrate of 1048 ml/min)
 - Filtration began when solution temperature was 56.7°C
- [00697] Reduction spent solution:

- 3.55 min filtration for 3093ml of Reduction solution (flowrate of 871ml/min)
- Filtration began when solution temperature was 56.1°C

[00698] Rinse filtrations:

- R4 rinse 1: 2.95 min filtration for 2200ml (flowrate of 746 ml/min)
- 5 - R4/R6/R2 rinse 2: 2.95 min filtration for 2200ml (flowrate of 746 ml/min)
- R4 rinse 3: 3.2 min filtration for 2200ml (flowrate of 688 ml/min)

[00699] Observations:

[00700] Reduction filtration did not have a proper cake due to agitator placement.

10 [00701] FRA 06: 3rd Party Gold

[00702] Experiment parameters:

[00703] 436g of unrefined gold from 3rd Party was leached and reduced in respective reactors 1 and 6.

[00704] Leach Filtration setup was as follows:

- 15 - Leach solution filtered through a cartridge filter (3-micron cartridge filter)
- The 10" cartridge filter wasn't used.

[00705] Reduction Filtration setup was as follows:

- Filter reactor with 0.45-micron PTFE, 0.45-micron PP, and 5-micron PTFE frit (order is from top to bottom)
- 20 - Kidney looping of filtrate for 10 min
- Only the reduction reactor filter was used in this step. The solution did not touch filter 11.
- Spent solution went through a cartridge filter (3 micron)
- Rinse solution went through a cartridge filter (3 micron)

25 [00706] Result:

[00707] Leach Filtration:

- 1 min filtration for 2182ml of leach solution (flowrate of 2182 ml/min)
- Filtration began when solution temperature was 55°C

[00708] Reduction spent solution:

- 30 - 4.8 min filtration for 3070ml of Reduction solution (flowrate of 640ml/min)
- Filtration began when solution temperature was 53°C

[00709] Rinse filtrations:

- R4 rinse 1: 2.85 min filtration for 2183ml (flowrate of 766 ml/min)
- R4/R6/R2 rinse 2: 2.6 min filtration for 2183ml (flowrate of 840 ml/min)
- R4 rinse 3: 3.2 min filtration for 2183ml (flowrate of 682 ml/min)

5 [00710] Tabulated Results of Filtration Test

Leach Reactor				Filter Reactor			
	m _{Au} (g)	Scale (L)	Total Scale (L) Leach + V _T	Filter Media/Sizes/et c.	Final Gold Purity (%)	Gold Account- ability (%)	Notes
FRA 01	235	1.175	1.51	2 µm USALAB paper, 5 µm frit	99.9903%	99.26%	Filter reactor commissioning, 2 micron paper broke up and contaminated gold
FRA 02	420	2.10	2.81	5 µm frit only	99.9975%	98.15%	Commissioning at 60% gold loading, reactor agitator set up sub- optimal in leach stage (~35g/420g Au left unleached)
FRA 03	420	2.10	2.96	0.45 µm PTFE hydrophillic, 0.45 µm PP weakly hydrophobic, 5 µm frit from FRA01 & 02	99.9988%	99.65%	Used vibratory agitator, leaching complete within 6 minutes
FRA 04	200	1.0	1.46	0.45 µm PTFE hydrophillic, 0.45 µm PP weakly hydrophobic, 5 µm frit (same as FRA03) Changed filter 1301 from polishing cartridge to large	99.8791%	100.51%	Gold pre burned in oven at 400°C for ~1 hour. 20% overdose of oxidant, some undissolved Au due to particle size (un sieved) Leach - 16 minutes, reduction - 2 hours 15 minutes
FRA 05	440	2.2	2.98	0.45 µm PTFE hydrophillic, 0.45 µm PP weakly hydrophobic, 5 µm frit (same as FRA03)	99.9924%	97.85%	Gold pre burned in oven at 400°C for ~1 hour. Half of input gold is from FRA04, re- refining with the un- refined portion of 3 rd

Leach Reactor				Filter Reactor			
	m_{Au} (g)	Scale (L)	Total Scale (L) Leach + V_T	Filter Media/Sizes/et c.	Final Gold Purity (%)	Gold Account- ability (%)	Notes
				Added filter 2303 to leach filter assembly (polishing)			party's burned gold, poor agitation in Reduction
FRA 06	436	2.18	2.96	0.45 μ m PTFE hydrophillic, 0.45 μ m PP weakly hydrophobic, 5 μ m frit (same as FRA03) Added filter 2303 to leach filter assembly (polishing)	99.9962%	99.68%	Recombined Au from FRA05, lab experiments, and lab aqua regia collection to re-refine

[00711] **Modification - O-Ring and Agitation System**

[00712] In one or more embodiments of the system described herein, an O-ring was added to an outlet plug of at least the leach reactor 1. The O-ring was added to reduce or prevent reduced precious metal, such as gold, from piling up, collecting, and getting trapped at the outlet of the Leach Reactor 1. An example of this is depicted in Figure 4. Figure 4A shows the bottom half 30 of a reactor, with plug 31 in the reactor outlet, and reduced precious metal 32 collecting between the walls of the outlet and the plug. In Figure 4B shows the bottom half 30 of the reactor, with plug 31 in the reactor outlet, and O-ring 33 coupled to the end of plug 31, which fits in the space between the walls of the outlet and the plug, preventing the collection of precious metals therebetween.

[00713] In one or more embodiments of the system described herein, agitator system comprises a vibratory agitator that - like the O-ring modification - may prevent precious metal such as gold from falling into voids within the reactor, which may aid leaching efficiency. Prior to using vibratory agitation, a 4" outer diameter agitator was used having 4 blades set at 60° made from Polytetrafluoroethylene (PTFE) from Chem Glass. Due to the large outer diameter, it was observed that the agitator created a dead zone directly below itself. Such agitation dead zones may result in gold remaining unleached. For example, it was observed that ~9% of gold may remain unleached due to agitation dead zones.

[00714] **Working Example**

[00715] The following describes an example of a refining experiment run with the system as described herein.

	Amount	Unit	Measured Mass (kg)	Notes
Condition considerations: Pressure: PSV set at 2.5 PSIG in leach reactor, 0.33 PSIG in reduction reactor, 50psi in liquid lines if cartridge filter plugs off Gases: Acidic vapor, Cl₂, ClO₂ Temperature: -PML: 70°C - Reduction: 60-70°C Runaway reactions: - Leach: Temp >75°C, Add cooling water to heating jacket - Reduction: Temp >70°C, STOP heating belt and wait until Temp < 65 to start heating belt Process sign off				
<i>Mass of Gold Powder</i>	436.37	g		
<i>Mass of filter system 20 comprising 0.45µm PTFE filter, 0.45µm PP filter, 5µm PTFE frit</i>	64.925	g		5µm PTFE frit = 62.900g 0.45µm PTFE = 1.198g 0.45µm PP = 0.827g
<i>Mass of 1302 cartridge filter (for example, Filter 3* in Figure 1)</i>	8.345	g		
<i>Mass of 1301 canister filter (for example, Filter 3* in Figure 1)</i>		g		
<i>Mass of 2302 cartridge filter (for example, Filter 11 in Figure 1)</i>	9.083	g		
<i>Mass of 2303 cartridge filter (for example, Filter 11 in Figure 1)</i>	8.704	g		
<i>Mass of centering ring (for example, see Figure 2)</i>	51.103	g		
Reducing Mixture R6 - Reactor 9				

	Amount	Unit	Measured Mass (kg)	Notes
Pour reducing mixture into reactor 9 (Note that, for this run, a previously prepared reducing mixture was used. Otherwise, this would start with heating the reagent make-up reactor)		ml		~1000ml
Start reactor R6 Makeupheaters ** Setpoint: T = 30°C				
Pump water/aqueous solution R4 via pump 8 into R6 Makeup reactor 9	500	ml	546	
Start Agitation		RPM		
Dose solid reductant R5 into reactor 9 via solids dosing system (EziDock)	213	g		
Pour water/aqueous solution R4 into R6 Makeup reactor 9 via EziDock	1,000	ml	1000	
Agitate for 60 min OR until R5 is fully dissolved				
Precious Metal Leach Reaction - Reactor 1				
Start reduction reactor 6 heat belt ** Setpoint: T = 25°C				
Pump 65% chemical R1 (solvent) to reactor 1	1004	ml	1099g	Dose mass: 1037g
Pump chemical R2 (acid) to reactor 1	960	ml	1114g	Dose mass: 1143g
Ensure temp of Leach > 22°C			28.5C	
Start Agitation	2.5	mm		Vibratory Agitator ESR 2000 - 81.9
Add in solid Au feedstock to reactor 1				**Reactor unsealed until t=18min
Start chemical R3 (oxidant) dosing pump: t = 0	43.6	ml/min		**oxidant scale errored out
t = 5 min: STOP R3 pump	218	ml	230ml dosed (visual check)	Dose mass: 306g
t = 8min: Check for residual gold				No agitation increase
IF residual gold: Increase agitation until t=15min				
Visually inspect for, and visually confirm gold dissolution.				

	Amount	Unit	Measured Mass (kg)	Notes
Pump R2 to reactor 1		ml		no additional doses
Pump R3 to reactor 1		ml		
Sample solution @ end of reaction				t=25 min
Pump pregnant leached solution to reduction reactor 6 through cartridge filters of filter system 20 ** Timer On!			55C	1:00 min filtration
Pump R1 to reactor 1 through to filter system 20.	250	ml	266g	Dose mass: 258g
Reduction Reactor 6				
Ensure all of leach reactor 1 leached solution has been pumped and lines are fully drained	2,455	ml		
Start Agitation	200	RPM	47C	
Confirm agitation through reactor glass & take heat belt off				Reduction reactor thermometer faulty
If Temp < 35°C, pump reducing mixture R6 into reactor 6	615	ml		34.4C
Once all R6 in: t = 0				
Increase reactor heat belt once Temp plateaus ** Setpoint: T = 63°C			Tmax = 66.8C	heat belt placed on reactor at 60.6C on exotherm ramp Jacket heat on at 12min (65.4C)
Sample: t = 30 min and determine Au concentration in solution to assess reduction efficiency.				
DIRECTION: Pump R6 into reactor 6	13.6	ml	13.23ml dosed at t=40 min	
t = 60 min: Stop agitation & turn off heat belt				
Sample: t = 60 min and determine Au concentration in solution to assess reduction efficiency.				
DIRECTION: Pump R6 into reactor 2701	20.0	ml		increased agitation to 250 RPM, soln bypassed frit

	Amount	Unit	Measured Mass (kg)	Notes
Sample: $t = 80$ min and determine Au concentration in solution to assess reduction efficiency.				
Pump spent leached solution to kidney loop (otherwise referred to second polishing filtering system comprising filter system 20 and pump 7 for 10 min ** Timer On!			55.9C	
Begin Filtration:				
Pump spent solution to spent solution storage tank through polishing filter 11 ** Timer On!			4:48	
Rinse 1: Pump R4 (water/aqueous solution) into reactor 6	2,183	ml	2138g	Dose mass: 2183g
Start Agitation for 2 min	300	RPM		
Pump Rinse 1 to kidney loop for 3 min ** Timer On!				
Pump Rinse 1 to AQ waste storage tank through polishing filter 12 ** Timer On!			2:51	
Rinse 2 - Pump following:				
Pump R4 into reactor 6	918	ml	900g	Dose mass: 918g
Start Agitation	300	RPM		
Pump R6 into reactor 6	1,174	ml		
Pump R2 into reactor 6	91	ml	105g	Dose mass: 108g
Agitate for 10 min				
Stop agitation and Sample				
Pump Rinse 2 to kidney loop for 3 min ** Timer On!				
Pump Rinse 2 to AQ waste storage tank through polishing filter 12 ** Timer On!			2:36	
Rinse 3: Pump R4 into reactor 6	2,183	ml	2126g	Dose mass: 2183g
Start Agitation for 2 min	300	RPM		

	Amount	Unit	Measured Mass (kg)	Notes
Pump Rinse 3 to kidney loop for 3 min ** Timer On!				
Pump Rinse 3 to AQ waste storage tank through polishing filter 12 ** Timer On!			3:12	
Collect Gold from filter and dry				
Pump R1 to reactor 1 through to filter 3, collect solution in a labeled container for the lab	500	ml	537g	Dose mass: 516g
Pump water (>1L) to reactor 1 through to filter 3, collect solution in a labeled container for the lab ** WEIGHT before and after	1000	ml		

[00716] Tabulated Results From Working Example

[00717] Shown below.

Rinse		Concentration of Metals in Solution (mg/L, ICP-OES)																	
Sample Identification	V _i (mL)	V ₂ (mL)	V ₁ (mL)	V _{total} (mL)	Au (mg/L)	Pt (mg/L)	Pd (mg/L)	Rh (mg/L)	Sn (mg/L)	Pb (mg/L)	Ag (mg/L)	Cu (mg/L)	Fe (mg/L)	Zn (mg/L)	Ni (mg/L)	Co (mg/L)	Cr (mg/L)	Mn (mg/L)	Al (mg/L)
Z1		2183			2183														
T	91	918	1174		2183	831	0.0	0.2	0.2	2.5	1.7	12.3	5.1	0.7	8.7	0.6	0.0	0.5	0.1
Z2		2183			2183														
Combined					6549														

Saturated T Gold Reduction										Concentration of Metals in Solution (ICP-OES)									
Sample Identification	m(g)	V _i (mL)	V ₁ Calculated (mL)	V _{total} (mL)	Au (mg/L)	Pt (mg/L)	Pd (mg/L)	Rh (mg/L)	Sn (mg/L)	Pb (mg/L)	Ag (mg/L)	Cu (mg/L)	Fe (mg/L)	Zn (mg/L)	Ni (mg/L)	Co (mg/L)	Cr (mg/L)	Mn (mg/L)	Al (mg/L)
Initial	87.33	615		2344.5	167986	0.0	0.3	0.1	13.3	0.4	13.4	2.2	0.8	1.1	0.3	0.0	0.8	0.1	0.0
30 min	1.9	13.2	13.6	2858.5	3289	0.0	0.4	0.1	1.7	0.1	11.0	6.6	0.0	3.6	0.0	0.0	0.4	0.0	1.1
80 min	1.4	20.0	10.0	2972.7	2378	0.0	0.3	0.1	2.0	0.3	11.0	7.8	1.6	2.3	0.4	0.0	0.7	0.0	2.2
80 min				2992.7	2105	0.0	0.3	0.0	1.5	0.0	10.3	3.0	0.0	5.1	0.4	0.0	0.8	0.1	0.0
Sampled from top of filter reactor, centrifuged before preparing ICP sample																			

Cold refining leach, 30% A ⁺ and Z added as a 65% A mixture							Concentration of Metals in Solution (mg/L, ICP-OES)														
Sample Identification	m _{gold} (g)	V _A (mL)	V _B (mL)	V _Z (mL)	V _W (mL)	V _{total} (mL)	Au	Pt	Pd	Rh	Sn	Pb	Ag	Cu	Fe	Ni	Co	Cr	Mn	Al	
Initial	436.371	653	860	351	0	1964.0															
Dosing Complete (5 min)	436.371					2182.0															
Filtrate (25 min)	436.371					2182.0	180495	0.0	0.4	0.1	14.3	0.4	14.4	2.4	0.9	1.2	0.3	0.0	0.6	0.1	
Filtrate + A Flush, est.	436.371	163				88	2344.5	167986	0.0	0.3	0.1	13.3	0.4	13.4	2.2	0.8	1.1	0.3	0.0	0.6	

[illegible][illegible]

[00718] The embodiments described herein are intended to be examples only. Alterations, modifications, and/or variations can be effected to the particular embodiments by those of skill in the art. The scope of the claims should not be limited by the particular
5 embodiments set forth herein, but should be construed in a manner consistent with the specification as a whole.

[00719] The aspects, embodiments, and/or examples of the present disclosure being thus described, it should be recognized that said aspects, embodiments, and/or examples may be varied in ways that do not depart from the spirit and scope of the present disclosure, and
10 that said variations are intended to be included within the scope of the following claims.

[00720] All publications, patents and patent applications mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication patent, or patent application was specifically and individually indicated to be incorporated by reference.

WHAT IS CLAIMED IS:

1. A method of refining a precious metal, the method comprising:
forming a refining solution, the refining solution comprising an acid in a partially water-miscible or water-miscible solvent;
adding a precious metal to the refining solution;
dosing an oxidant into the refining solution;
leaching the precious metal into the refining solution; and
forming a leached solution comprising leached precious metal.
2. The method of claim 1, wherein dosing an oxidant into the refining solution comprises:
continuously dosing the oxidant into the refining solution over a period of time; and/or
dosing the oxidant at time intervals.
3. The method of claim 2, wherein continuously dosing the oxidant into the refining solution over a period of time comprises:
dosing the oxidant into the refining solution for the duration of leaching the precious metal into the refining solution; or
dosing the oxidant into the refining solution for a period of time that is less than the duration of leaching the precious metal into the refining solution.
4. The method of claim 1 or 2, wherein dosing the oxidant at time intervals comprises:
adding a first dose of the oxidant to the refining solution when forming the refining mixture; and
adding subsequent doses of the oxidant to the refining solution at intervals of time after adding the first dose.
5. The method of claim 4, wherein adding subsequent doses of the oxidant comprise adding two or more additional doses of oxidant.
6. The method of claim 4 or 5, wherein each of the intervals of time after adding the first dose is about 1 min to about 5 min; or about 1 min to about 4 min; or about 1 min to about 3 min; or about 1 min to 2 min; or about 1 min.

7. The method of any one of claims 1 to 6, further comprising filtering the leached solution to remove undissolved solids, precipitated solids, or a combination thereof.
8. The method of any one of claims 1 to 7, further comprising
adding a reductant to the leached solution; and
reducing the leached precious metal; and
precipitating reduced precious metal.
9. The method of claim 8, wherein adding a reductant to the leached solution further comprises
adding a first dose of a base to the leached solution a first period of time after adding the reductant; and
optionally adding a second dose of the base a second period of time after adding the first dose of base.
10. The method of claim 9, wherein the first period of time and/or the second period of time is about 1 to about 10 min; or about 3 to about 10 min; or about 7 to about 10 min.
11. The method of any one of claims 8 to 10, wherein the reductant comprises thiourea, sodium metabisulfite, sodium sulfite, or a combination.
12. The method of any one of claims 8 to 11, wherein the reductant comprises an aqueous solution of thiourea.
13. The method of any one of claims 8 to 12, wherein adding a reductant to the leached solution and reducing the leached precious metal comprises heating the leached solution.
14. The method of claim 13, wherein heating the leached solution comprises bring the leached solution to a temperature above ambient temperature and below the boiling point of the leached solution.

15. The method of claim 13 or 14, wherein heating the leached solution comprises bringing the leached solution to a temperature of about 35°C to about 75°C; or about 40°C to about 70°C; or about 45°C to about 65°C; or about 50°C to about 65°C; or about 55°C to about 65°C; or about 60°C.
16. The method of any one of claims 8 to 15, further comprising separating the reduced precious metal from the leached solution.
17. The method of any one of claim 8 to 16, further comprising washing the reduced precious metal with water, an aqueous solution, or a combination thereof.
18. The method of any one of claim 8 to 17, further comprising rinsing the reduced precious metal with a rinse solution to form a refined precious metal.
19. The method of claim 18, wherein the rinse solution comprises a rinse acid, a rinse complexing agent, or a combination thereof.
20. The method of claim 18 or 19, wherein the rinse solution comprises a rinse acid and a rinse complexing agent.
21. The method of claim 19 or 20, wherein the rinse acid comprises acetic acid, glacial acetic acid, hydrochloric acid, nitric acid, sulfuric acid, or a combination thereof.
22. The method of any one of claims 19 to 21, wherein the rinse complexing agent comprises a thiourea, a thiosulfate, or a combination.
23. The method of any one of claims 18 to 22, wherein the rinse solution comprises an aqueous solution of thiourea and hydrochloric acid.
24. The method of any one of claims 18 to 23, wherein rinsing the reduced precious metal with a rinse solution comprises heating the rinse solution.

25. The method of claim 24, wherein heating the rinse solution comprises bringing the rinse solution to a temperature above ambient temperature and below the boiling point of the rinse solution.
26. The method of claim 24 or 25, wherein heating the rinse solution comprises bring the rinse solution to a temperature of about 35°C to about 75°C; or about 40°C to about 70°C; or about 45°C to about 65°C; or about 50°C to about 65°C; or about 50°C to about 60°C; or about 60°C.
27. The method of any one of claims 18 to 26, further comprising washing the refined precious metal with water, an aqueous solution, or a combination thereof.
28. The method of any one of claims 1 to 27, wherein forming the refining solution, adding the precious metal to the refining solution, and dosing the oxidant into the refining solution comprises:
combining the acid, a first dose of the oxidant, and a ligand source in the partially water-miscible or water-miscible solvent; and then
adding the precious metal.
29. The method of claim 28, wherein the ligand source comprises a chloride salt.
30. The method of claim 28 or 29, wherein the ligand source comprises MgCl_2 , AlCl_3 , CaCl_2 , or a combination thereof.
31. The method of any one of claims 1 to 27, further comprising recharging the refining solution with a final dose of the oxidant and a second dose of the acid.
32. The method of claim 31, further comprising
adding a second oxidant and a polyatomic salt to the leached solution to precipitate contaminants from the leached solution.
33. The method of claim 32, wherein the polyatomic salt comprises an ammonium salt.

34. The method of claim 32 or 33, wherein the polyatomic salt comprises ammonium chloride, ammonium sulfate, ammonium nitrate, or combinations thereof.
35. The method of any one of claims 32 to 34, wherein the second oxidant comprises HNO_3 , H_2O_2 , O_2 , bubbled air, I_2 , NaClO_2 , NaClO_3 , KClO_3 , NH_4ClO_3 , NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , $\text{Ca}(\text{ClO})_2$, Cl_2 , CuCl_2 , FeCl_3 , CaO_2 , sodium iodate, potassium iodate, manganese dioxide, perchloric acid, or combinations thereof.
36. The method of claim 35, wherein the second oxidant comprises KClO_3 , NH_4ClO_3 , NaClO_3 .
37. The method of claim 35 or 36, wherein the second oxidant comprises NaClO_3 .
38. The method of any one of claims 1 to 37, further comprising pre-rinsing the precious metal before adding the precious metal to the refining solution.
39. The method of claim 38, wherein pre-rinsing the precious metal comprises rinsing the precious metal with
- the partially water-miscible or water-miscible solvent;
 - acetic acid, glacial acetic acid, or a combination thereof;
 - water, an aqueous solution, or a combination thereof; and/or
 - the rinse solution of any one of claims 18 to 26.
40. The method of any one of claims 1 to 39, wherein the acid of the refining solution comprises HCl , HBr , HI , chlorous acid, chloric acid, bromous acid, bromic acid, iodosous acid, iodic acid, perchloric acid, sulfuric acid, nitric acid, oxalic acid, phosphoric acid, methanesulfonic acid, citric acid, an organic acid, or combinations thereof.
41. The method of any one of claims 1 to 40, wherein the acid of the refining solution comprises HCl , HBr , HI .
42. The method of any one of claims 1 to 41, wherein the acid of the refining solution comprises HCl .

43. The method of any one of claims 1 to 42, wherein the oxidant of the refining solution comprises HNO_3 , H_2O_2 , O_2 , bubbled air, I_2 , NaClO_2 , NaClO_3 , KClO_3 , NH_4ClO_3 , NaClO , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , $\text{Ca}(\text{ClO})_2$, Cl_2 , CuCl_2 , FeCl_3 , CaO_2 , sodium iodate, potassium iodate, manganese dioxide, perchloric acid, or combinations thereof.
44. The method of any one of claims 1 to 43, wherein the oxidant comprises KClO_3 , NH_4ClO_3 , NaClO_3 .
45. The method of any one of claims 1 to 44, wherein the oxidant comprises NaClO_3 .
46. The method of any one of claims 1 to 45, wherein the partially water-miscible or water-miscible solvent comprises glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, or a combination thereof.
47. The method of any one of claims 1 to 46, wherein the partially water-miscible or water-miscible solvent comprises aqueous solutions of glacial acetic acid, acetic acid, ethyl acetate, acetonitrile, THF, or a combination thereof.
48. The method of any one of claims 1 to 47, wherein the partially water-miscible or water-miscible solvent comprises: glacial acetic acid; acetic acid; an aqueous solution of glacial acetic acid; and aqueous solution of acetic acid; or a combination thereof.
49. The method of any one of claims 1 to 48, wherein the partially water-miscible or water-miscible solvent comprises glacial acetic acid; an aqueous solution of glacial acetic acid; or a combination thereof.
50. The method of claim 48 or 49, wherein the aqueous solution of glacial acetic acid comprises about 20% by volume to about 30% by volume glacial acetic acid.
51. The method of any one of claims 1 to 50, wherein the precious metal comprises Au, Pt, Pd, Rh, Ru, Ir, Os, or a combination thereof.

52. The method of any one of claims 1 to 51, wherein the precious metal comprises Au, Pd, Pt, Rh, or a combination thereof.
53. The method of any one of claims 1 to 52, wherein the precious metal comprises Au.
54. The method of any one of claims 1 to 53, wherein the refined precious metal has a purity of $\geq 99\%$, $\geq 99.9\%$, or $\geq 99.99\%$.
55. A system for refining a precious metal, the system comprising:
- a leach reactor,
 - the leach reactor having a first agitator and a first port for dosing a precious metal into the leach reactor,
 - the leach reactor being in fluid communication with a leach dosing system for dosing a refining solution into the leach reactor; and
 - a reduction reactor in fluid communication with the leach reactor,
 - the reduction reactor having a second agitator, and being in fluid communication with
 - a reducing dosing system for dosing a reducing mixture into the reduction reactor, and
 - a rinsing system for dosing a rinse solution into the reduction reactor;
- the precious metal and refining solution being dosed into the leach reactor and agitated to leach the precious metal into the refining solution and form a leached solution comprising a leached precious metal;
- the leached solution being transferred to the reduction reactor; the reducing mixture being dosed into the reduction reactor; and being agitated to reduce the precious metal and form precipitated precious metal.
56. The system of claim 55, further comprising a first polishing filter system in fluid communication with the leach reactor, the first polishing filter system comprising a filter in fluid

communication with the leach reactor and a first transfer pump, the transfer pump being in fluid communication with the reduction reactor;

wherein:

the leached solution being transferred to the reduction reactor comprises

filtering the leached solution through the polishing filter system to remove insoluble impurities from the leached solution.

57. The system of claim 55 or 56, further comprising a first polishing filter system coupled to leach reactor, the first polishing filter system comprising a filter system coupled to the leach reactor and a first transfer pump, the transfer pump being in fluid communication with the reduction reactor;

wherein:

the leached solution being transferred to the reduction reactor comprises

filtering the leached solution through the polishing filter system to remove insoluble impurities from the leached solution.

58. The system of claim 55 or 56, further comprising a second polishing filter system coupled to the reduction reactor, the second polishing filter system comprising a filter system coupled to the reduction reactor in fluid communication with a second transfer pump, the transfer pump being in fluid communication with the reduction reactor;

wherein

reducing the precious metal and forming precipitated precious metal comprises

forming a spent leached solution and precipitated precious metal mixture, and filtering the mixture through the second polishing filter system to remove the precipitated precious metal from the mixture.

59. The system of any one of claims 55 or 58, further comprising a second polishing filter in fluid communication with the reduction reactor, the second polishing filter system comprising a filter in fluid communication with reduction reactor and a second transfer pump, the transfer pump being in fluid communication with the reduction reactor;

wherein

reducing the precious metal and forming precipitated precious metal comprises

forming a spent leached solution and precipitated precious metal mixture, and filtering the mixture through the second polishing filter system to remove the precipitated precious metal from the mixture.

60. The system of claim 58 or 59, wherein filtering the mixture through the second polishing filter system to remove the precipitated precious metal from the mixture comprises recycling the filtered spent leached solution back to the reduction reactor.

61. The system of any one of claims 55 to 60, wherein filter system comprises a base to couple to the reactor; and a filter medium coupled to the base.

62. The system of claim 61, wherein the filter medium comprises a frit and/or optionally least one filter paper.

63. The system of claim 62, wherein the frit and/or optionally least one filter paper comprises a polyalkylene, a polyfluorinated polymer, or a combination thereof.

64. The system of any one of claims 61 to 63, wherein the frit comprises a about 1 micron to about 5 micron rating.

65. The system of any one of claims 61 to 64, wherein the at least one filter paper comprises a about 0.45 to about 3 micron rating.

66. The system of any one of claims 55 to 65, wherein the leach dosing system comprises a first reagent drum in fluid communication with a first reagent pump, the first reagent drum comprising the refining solution and the first reagent pump in fluid communication with the leach reactor.

67. The system of any one of claims 55 to 66, wherein the refining solution comprises a solvent, an acid, and an oxidant, and the leach dosing system comprises: a leach solvent drum in fluid communication with a leach solvent pump, the leach solvent pump being in fluid communication with the leach reactor;

a leach acid drum in fluid communication with a leach acid pump, the leach acid pump being in fluid communication with the leach reactor; and

a leach oxidant drum in fluid communication with a leach oxidant pump, the leach oxidant pump being in fluid communication with the leach reactor;

wherein:

the solvent, acid, and oxidant are separately dosed into the leach reactor to form the refining in the leach reactor.

68. The system of any one of claims 55 to 67, wherein the reducing dosing system comprises a second reagent drum in fluid communication with a second reagent pump, the second reagent drum comprising the reducing mixture and the second pump being in fluid communication with the reduction reactor.

69. The system of any one of claims 55 to 63, wherein the reducing mixture comprises a reductant, optionally in solution, and the reducing dosing system comprises:

a reagent make-up reactor,

the reagent make-up reactor having an agitator and a first port for dosing the reductant into the mixing reactor,

the reagent make-up reactor being in fluid communication with the reduction reactor; and

an optional solution drum in fluid communication with an optional solution pump, the solution pump being in fluid communication with the reagent make-up reactor;

wherein:

the reductant and optional solution are dosed into the reagent make-up reactor and agitated to form the reducing mixture.

70. The system of claim 69, wherein the reducing mixture comprises a reductant in solution, and the system comprises the solution drum and pump.

71. The system of claim 69 or 70, wherein the reducing mixture comprises a reductant in aqueous solution, and the solution drum and pump comprise an aqueous solution drum and an aqueous solution pump.

72. The system of any one of claims 55 to 71, wherein the rinse solution comprises a rinse acid and a rinse complexing agent, and the rinsing system comprises:

a third reagent drum in fluid communication with a third reagent pump, the third reagent drum comprising a rinse acid and the third pump being in fluid communication with the reduction reactor; and

a fourth reagent drum in fluid communication with a fourth reagent pump, the fourth reagent drum comprising a rinse complexing agent and the fourth pump being in fluid communication with the reduction reactor;

wherein:

rinse complexing agent and rinse acid are dosed into the reduction reactor to form the rinse solution, and the rinse solution is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal.

73. The system of claim 72, wherein the fourth reagent drum in fluid communication with the fourth reagent pump, the fourth reagent drum comprising a rinse complexing agent and the forth pump being in fluid communication with the reducing reactor comprises

the reducing dosing system,

wherein

the solution drum and pump are an aqueous solution drum and an aqueous solution pump, and

aqueous solution is dosed into the reduction reactor, the reductant is dosed into the reduction reactor, and the rinse acid is dosed into the reduction reactor, to form the rinse solution, and the rinse solution is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal.

74. The system of claim 72 or 73, further comprising dosing additional aqueous solution into the reduction reactor and flowing through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal.

75. The system of any one of claims 72 to 74, wherein the third reagent drum in fluid communication with the third reagent pump, the third reagent drum comprising the rinse acid and the third pump being in fluid communication with the reduction reactor comprises

the leach acid drum in fluid communication with a leach acid pump, the leach acid pump being diverted to be in fluid communication with the reduction reactor.

76. The system of any one of claims 55 to 75, wherein the rinse solution comprises a rinse acid and a rinse complexing agent, the rinse complexing agent comprising the reducing mixture, and the rinsing system comprises:

a third reagent drum in fluid communication with a third reagent pump, the third reagent drum comprising the rinse acid and the third pump being in fluid communication with the reduction reactor;

a fourth reagent drum in fluid communication with a fourth reagent pump, the fourth reagent drum comprising an aqueous solution and the forth pump being in fluid communication with the reducing reactor; and

the reducing dosing system;

wherein:

the aqueous solution is dosed into the reduction reactor, the reducing mixture is dosed into the reduction reactor, and the rinse acid is dosed into the reduction reactor, to form the rinse solution, and

the rinse solution is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal; and optionally

an additional dose of aqueous solution is dosed into the reduction reactor and is flowed through the precipitated precious metal collected within the second polishing filter system to rinse the precipitated precious metal.