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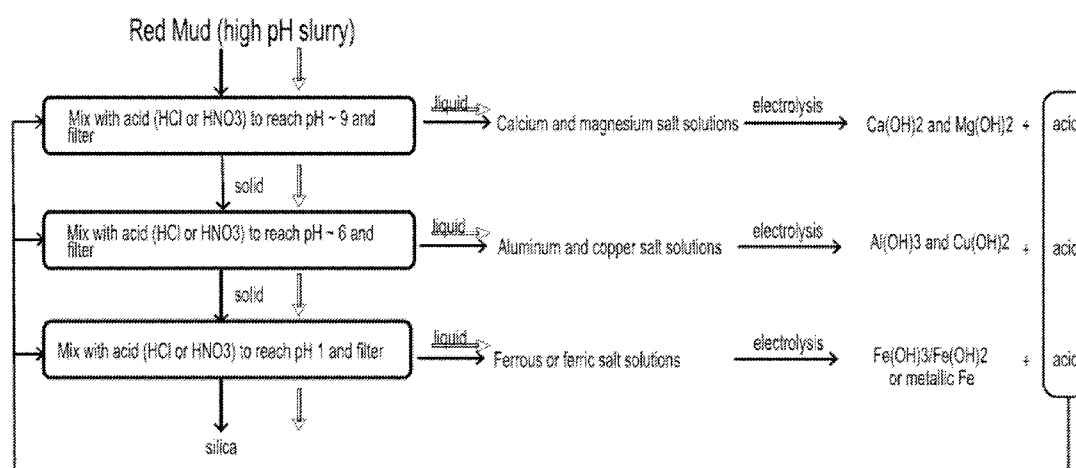
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(54) Title: METHODS OF REMEDIATING WASTE AND SYSTEMS THEREOF

FIG. 1



(57) Abstract: Provided herein are methods of reducing the chemical content such as metal, sulfur, phosphorus, and/or organic content of waste. The methods and systems include contacting waste with an acid or base to neutralize the waste.

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METHODS OF REMEDIATING WASTE AND SYSTEMS THEREOF

FIELD

[0001] The present disclosure generally relates to a method of reducing chemical content such as metals, sulfur, phosphorus, and/or organic content in waste and systems thereof.

BACKGROUND

[0002] Mine drainage, mine tailings, agricultural runoff, desalination brine, manufacturing waste, and industrial waste can contain high levels of chemical content such as metals, as well as sulfur, phosphorus, and/or other organic materials, many of which are toxic, persistent, and resist conventional biological and chemical waste treatment and as such are undesirable to have in a waste stream.

[0003] With increasing world population comes increased volumes of waste, tighter wastewater quality regulations, increased cost of producing clean water, aging wastewater treatment infrastructure and potential clean water shortages. The human and environmental impact of these types of waste are significant and current mitigation strategies are insufficient.

SUMMARY

[0004] Provided herein are methods and systems for reducing chemical content such as metals, sulfur, phosphorus, and/or organic content in waste. The systems and methods described herein can have several advantages over the conventional methods of reducing such chemical content such as metals, sulfur, phosphorus, and/or organic content in waste, including (for example), significantly reducing the chemical content such as metals, sulfur, phosphorus, and/or organic content in the waste, using less energy (e.g., net energy neutral), producing less CO₂ (e.g., carbon neutral) or even being net carbon negative (e.g., sequestering CO₂), and providing a regenerative process to reuse byproducts of the process in the process.

[0005] In general, this disclosure relates to processes and systems for reducing chemical content such as metals, sulfur, phosphorus, and/or organic content in waste and/or reducing the environmental impact of waste. In some embodiments, the chemical content is comprised of ions. In some embodiments, the chemical content is comprised of metallic ions, for example ions of sodium, potassium, magnesium, calcium, tin, lead, iron, cobalt, nickel, copper, zinc, palladium, and cadmium. In some embodiments, the chemical content is comprised of ions of sulfur, phosphorus, for example phosphates or sulfates. In some embodiments, the chemical content is comprised of organic compounds, for example phenol derivatives.

[0006] A method of reducing chemical content in acidic mine waste comprising one or more target ions, the method comprising:

(a) contacting the acidic mine waste with a base to form modified acidic waste and optionally insoluble salts of one or more target ions;

(b) contacting the modified acidic waste with an electrolyzer to form (i) a base or a product comprising insoluble salts of one or more target ions, or metallic deposition on the cathode of one or more target ions, and (ii) an acid.

(c) optionally repeating step (a) at least once, wherein the base of repeated step (a) comprises the base of step (b)(i).

[0007] A method of reducing chemical content in acidic mine waste comprising one or more target ions, the method comprising:

(a) contacting the acidic mine waste with a base and carbon dioxide to form (i) insoluble carbonate salts of one or more target ions; and (ii) a solution rich in ions;

(b) contacting the solution rich in ions of step (a)(ii) with an electrolyzer to regenerate (i) a base and (ii) an acid; and

(c) optionally repeating steps (a) and (b), wherein the base of repeated step (a) comprises the regenerated base of step (b)(i).

[0008] A method of reducing chemical content in acidic mine waste comprising one or more target ions, the method comprising:

(a) contacting the acidic mine waste with an electrolyzer to form (i) an acid and (i) metal hydroxides or metallic deposition on the cathode of one or more target ions; and

(b) collecting the metal hydroxide or the metallic deposition of step (a).

[0009] A method of reducing chemical content in acidic mine waste, the method comprising:

contacting the acidic mine waste comprising one or more target ions with a base in an electrochemical cell to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, and the electrochemical cell regenerates the base and forms an acidic product comprising the one or more ions and optionally insoluble salts thereof;

wherein the electrochemical cell comprises an anode reservoir comprising an anode and the acid, and a cathode reservoir comprising a cathode and the base, wherein the anode reservoir and the cathode reservoir are separated by a separator.

[0010] A method of reducing the environmental impact of acidic mine waste, the method comprising:

(a) contacting the acidic mine waste comprising one or more target ions with a base to

form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof;

(b) contacting the modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, with an electrolyzer to regenerate the base and form an acidic product comprising the one or more ions and optionally insoluble salts thereof, and

(c) repeating step (a) at least once, wherein the base of repeated step (a) comprises the base of step (b).

[0011] A system for reducing chemical content in acidic mine waste, comprising:

an electrochemical cell configured to reduce chemical content in acidic mine waste, wherein the electrochemical cell comprises an anode reservoir comprising an anode and an acid, and a cathode reservoir comprising a cathode and a base, wherein the anode reservoir and the cathode reservoir are separated by a separator;

a contactor configured to input the acidic waste comprising one or more target ions into the cathode reservoir, wherein the cathode reservoir is configured to contact the acidic waste with the base to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, and the anode reservoir is configured to contact the modified acidic waste comprising the one or more ions with the acid to form an acidic product comprising the one or more ions and optionally insoluble salts thereof;

a first filtration system in contact with the cathode reservoir configured to filter out any insoluble salts from the modified acidic waste from the cathode reservoir; and

a second filtration system in contact with the anode reservoir configured to filter out any insoluble salts from the acidic product comprising the one or more ions and optionally insoluble salts thereof, from the anode reservoir.

[0012] Some embodiments provide a method of reducing the environmental impact of acidic waste comprising one or more of mining drainage, mine tailings, manufacturing waste, industrial waste, agricultural runoff, and brine, the method comprising:

(a) contacting the acidic waste comprising one or more target ions with a base to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof;

(b) contacting the modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, with an electrolyzer to regenerate the base and form an acidic product comprising the one or more ions and optionally insoluble salts thereof, and

(c) repeating step (a) at least once, wherein the base of repeated step (a) comprises

the base of step (b).

[0013] Other implementations of the above methods include corresponding systems and apparatus, configured to perform the actions of the methods. The details of one or more embodiments of the subject matter described in this specification are set forth in the accompanying drawings and the description below. Other features, aspects, and advantages of the subject matter will become apparent from the description, the drawings, and the claims.

DESCRIPTION OF DRAWINGS

[0014] FIG. 1 shows flow chart of treatment procedure 1 for removing metallic content from mine tailings.

[0015] FIG. 2 shows flow chart of treatment procedure 2 for removing metallic content from mine tailings.

[0016] FIG. 3 shows composition of an exemplary sample of acidic mine drainage.

[0017] FIG. 4 shows flow chart of treatment procedure 3 for removing metallic content from acidic mine drainage.

[0018] FIG. 5 shows flow chart of treatment procedure 4 for removing metallic content from acidic mine drainage.

[0019] FIGs. 6A and 6B shows an example of an H-type electrolyzer used in selected examples described herein.

[0020] FIGs. 7A and 7B show the cathode potential and power consumption over time of H-type electrolyzer having 0.1 M NiSO₄ in the catholyte.

[0021] FIG. 8 shows the concentration of Ni²⁺ over time in H-type electrolyzer 0.1 M NiSO₄ in the catholyte.

[0022] FIG 9 shows material deposited on the cathode established it to be 100% crystalline Ni, in the initial run with 0.1 M NiSO₄ in the catholyte.

[0023] FIGs. 10A and 10B show the three regions in cathode potential without potential cutoff, and cathode potential with cutoff, respectively.

[0024] FIGs. 11A and 11B show the energy consumption without and with cathode potential cutoff, respectively, for catholyte containing 0.1 M NiSO₄ + 0.1 M CoSO₄.

[0025] FIGs. 12A and 12B show Ni²⁺ and Co²⁺ concentration levels individually and collectively, respectively, in catholyte reservoir without potential cutoff.

[0026] FIGs. 13A and 13B show the combined metal deposition of the cathode after Ni /Co electrolysis with no potential cutoff.

[0027] FIGs. 14A and 14B show Ni^{2+} and Co^{2+} concentration levels individually and collectively, respectively, in catholyte reservoir with potential cutoff.

[0028] FIG. 15 shows deposition on the cathode of Ni /Co electrolysis run before potential cutoff.

[0029] FIG. 16 shows deposition on the cathode of Ni /Co electrolysis run after potential cutoff.

[0030] FIGs. 17A and 17B show cathode potential vs time and energy consumption, respectively, for the Fe plus Acid run.

[0031] FIGs. 18A and 18B show the UV-Vis traces for catholyte before run, after run, and of the anolyte, and the pH of catholyte and anolyte before and after of the Fe plus Acid run, respectively.

[0032] FIGs. 19A and 19B show Fe deposition on the cathode after the Fe plus Acid run immediately after reaction and 18 h after the reaction, respectively. Exposure to air oxidized the elemental iron.

[0033] FIGs. 20A and 20B show the scanning electron microscope/energy-dispersive X-ray spectroscopy (SEM-EDS) and elemental composition of metallic content, respectively, of the cathode of the Fe plus Acid electrolysis run shown in FIG. 19A.

[0034] FIGs. 21A and 21B show cathode potential and energy consumption, respectively, of Fe plus Cu plus Zn run.

[0035] FIGs. 22A and 22B show the UV-Vis traces for catholyte before run, after run, and of the anolyte, and the pH of catholyte and anolyte before and after of the of Fe plus Cu plus Zn run, respectively.

DETAILED DESCRIPTION

[0036] Various industries are under pressure from both stricter discharge standards and rising mitigation costs to eliminate recalcitrant wastewater pollutants prior to discharge, and to adopt on-site water reuse and recycling systems to avoid rising water supply and effluent discharge costs. However, current technologies suffer from numerous shortcomings. Thus, there is a need for cost-effective, sustainable water treatment technology that does not require the addition of chemicals and does not produce secondary pollution, is compliant with stringent water quality standards, and has minimal operational and maintenance requirements.

[0037] The present disclosure solves this problem using regenerative electrochemical processes to separate problematic waste components in a safe, cost-effective manner.

Definitions

[0038] To facilitate understanding of the disclosure set forth herein, a number of additional terms are defined below. Generally, the nomenclature and procedures described herein are those well-known and commonly employed in the art. Unless defined otherwise, all technical and scientific terms used herein generally have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Each of the patents, applications, published applications, and other publications that are mentioned throughout the specification and the attached appendices are incorporated herein by reference in their entireties.

[0039] The term “about” when referring to a number or a numerical range means that the number or numerical range referred to is an approximation, for example, within experimental variability and/or statistical experimental error, and thus the number or numerical range may vary up to $\pm 10\%$ of the stated number or numerical range.

[0040] The term “regeneration” as used herein refers to a step in a process for using the product of a particular step in the process as a reactant or starting material in another step in the process. For example, if compound A is formed from reacting compounds C and X, one of the products of the reaction $A+B \rightarrow C+D$, compound C, can be further reacted with X to provide A, the starting material for the A+B reaction. In some embodiments, the methods described herein utilize acid (or base) in the initial step(s) and acid (or base) is regenerated in later step(s). The regenerated acid (or base) can then be fed back into the method, providing a regenerative process after the initial input of acid (or base).

[0041] The term “electrochemical cell” as used here refers to devices and/or device components that perform electrochemistry. Electrochemical cells have two or more electrodes (e.g., a cathode and an anode) and one or more electrolytes.

[0042] The term “basic waste” as used herein refers to waste having a pH of greater than about 7.5 (e.g., 7.6, 7.8, 8, 8.5, 9, 9.5, 10, 10.5, 11, 11.5, 12, 12.5, 13, 13.5, or 14).

[0043] The term “contactor” as used herein refers to devices and/or device components that facilitate contact of one type of material, mixture, liquid or gas with another. Non-limiting examples of contactor devices and/or components include manual or servo-controlled pneumatically or electrically actuated ball valves, butterfly valves, plug valves, globe valves, gate valves, needle valves, solenoid valves, coaxial valves, and angle seat valves.

[0044] The term “modified waste” (e.g., modified basic waste or modified acidic waste) as used herein refers to waste having a pH in a range of about 6.5 to about 7.5 (e.g., 6.5, 6.75, 7, 7.25, or 7.5).

[0045] The term “acidic waste” as used herein refers to waste having a pH of less than about 6.5 (e.g., 6.4, 6.2, 6, 5.5, 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, 1, 0.5, or 0).

[0046] The term “chemical content” as used herein refers to the amount of soluble and/or insoluble ions, e.g. cations of metals and/or anions of sulfur, phosphorus, and/or organic compounds, and/or salts and/or complexes thereof, wherein the organic content includes organic pollutants or other organic contaminants including, but not limited to phenol derivatives. In other words, “chemical content” as used herein does not solely refer to metals, but also includes certain non-metallic elements and/or compounds that are present in the form of salts or complexes as described above. The chemical content can take the form of solids, liquids, and mixtures thereof, including emulsions, suspensions, solutions, and particulate mixtures (including very fine particles such as micro and nanoparticles).

[0047] The term “separator” as defined herein, refers to the material between the cathode and anode reservoirs in an electrochemical cell. Representative separators include, but are not limited to cation exchange membranes and anion exchange membranes.

[0048] The term “multi-ion sequential electrowinning” as used herein refers to the electrochemical process that separates different materials in space over may linked cells, or one cell in time via differences cell pH and/or cell voltage, analogous to a traditional distillation column that separates materials by boiling point. In a constant-current electrolysis (i.e., continuous multi-ion sequential electrowinning), voltage plateaus when one species is precipitating out and then rapidly increases until another species begins to precipitate.

[0049] The term “sequential electrolysis” as used herein refers to a process wherein a substrate is oxidized or reduced sequentially.

[0050] The term “concentration overpotential” as used herein refers to the equilibrium potential difference across a diffusion layer given a particular electrode reaction and density. The greater the potential difference, the greater the rate of corrosion experienced with a corresponding electrolyte.

[0051] The term “catholyte” as used herein refers to the electrolyte solution located in the cathode reservoir.

[0052] The term “anolyte” as used herein refers to the electrolyte solution located in the anode reservoir.

[0053] The term “ion” as used herein, refers to a species having a net electric charge due to loss or gain of one or more electrons; Non-limiting examples of ions include Cl^- , PO_4^{3-} , Na^+ , Fe^{3+} , Fe^{2+} , Mg^{2+} , K^+ , Ca^{2+} , and Pb^{2+} . Reference herein to ions of specific elements refers to all possible ions thereof; for example, ions of Cu include Cu^+ and Cu^{2+} . Non-limiting examples of

ions of sulfur include SO_4^{2-} and SO_3^{2-} . A “target ion” as used herein refers to an ion of an element targeted for removal from the waste stream.

Selected Methods

[0054] Some embodiments provide a method of reducing chemical content in basic waste, the method comprising:

(a) contacting the basic waste comprising one or more target ions with an acid to form modified basic waste comprising the one or more ions and optionally insoluble salts thereof;

(b) contacting the modified basic waste comprising the one or more ions and optionally insoluble salts thereof, with an electrolyzer to form a basic product comprising the one or more ions and optionally insoluble salts thereof, and regenerate the acid, and

(c) repeating step (a) at least once, wherein the acid of repeated step (a) comprises the acid from step (b).

[0055] In some embodiments, the basic waste or the acid waste is one or more of mining drainage, mine tailings, manufacturing waste, industrial waste, agricultural runoff, and brine. In some embodiments, the basic waste comprises one or more of mining drainage, mine tailings, manufacturing waste, industrial waste, agricultural runoff, and brine. In some embodiments, the acidic waste comprises one or more of mining drainage, mine tailings, manufacturing waste, industrial waste, agricultural runoff, and brine. In some embodiments, the basic waste is mining drainage. In some embodiments, the basic waste is mine tailings. In some embodiments, the basic waste is agricultural runoff. In some embodiments, the basic waste is manufacturing waste. In some embodiments, the basic waste is industrial waste. In some embodiments, the basic waste is brine (e.g., desalination brine). In some embodiments, the acidic waste is mining drainage. In some embodiments, the acidic waste is mine tailings. In some embodiments, the acidic waste is agricultural runoff. In some embodiments, the acidic waste is manufacturing waste. In some embodiments, the acidic waste is industrial waste. In some embodiments, the acidic waste is brine (e.g., desalination brine).

[0056] The mining drainage and/or mine tailings can include toxic or dangerous chemicals and/or metal ions. Non-limiting examples of ion contaminants in mining drainage and/or mine tailings includes ions of Fe, Al, Ni, Co, Zn, Mn, Ca, Mg, and sulfate. Non-limiting examples of sulfur, phosphorus, and/or organic content present in mining drainage and/or mine tailings include sulfates, sulfites, metal sulfides, hydrogen sulfide, or phosphate salts.

[0057] The agricultural runoff can include toxic or dangerous chemicals and/or metal ions.

Non-limiting examples of sources for agricultural runoff includes fertilization, pesticides, livestock manure, and wastewater from agricultural processes. Non-limiting examples of metal ions present in agricultural runoff includes ions of Cd, Pb, Cu, Zn, As, Ca, and Mg. Non-limiting examples of sulfur, phosphorus, and/or organic content present in agricultural runoff includes sulfates, sulfites, metal sulfides, hydrogen sulfide, polyphosphate, phosphate salts, and phenol derivatives.

[0058] The manufacturing/industrial waste can include toxic or dangerous chemicals and/or metal ions. Non-limiting examples of sources for manufacturing/industrial waste includes chemical manufacturing, leather tanning, battery manufacture or maintenance, equipment maintenance and repair or washing, and plating and electroplating. Non-limiting examples of metal ions present in manufacturing/industrial waste includes ions of Cd, Pb, Cu, Pd, Zn, Ni, Fe, Cr, and Mg. Non-limiting examples of sulfur, phosphorus, and/or organic content present in manufacturing/industrial waste include sulfates, sulfites, metal sulfides, or hydrogen sulfide, polyphosphate, phosphate salts, and phenol derivatives.

[0059] The brine can include desalination brine, and can include toxic or dangerous amounts of ions (e.g., metal ions). Non-limiting examples of ions present in brine include ions of Cl, Na, Ca, Mg, Cu, Ni, Fe, Cr, and Mo. Non-limiting examples of sulfur, phosphorus, and/or organic content present in brine include sulfates and phosphates.

[0060] Some embodiments provide a method of reducing chemical content in basic waste comprising one or more target ions, the method comprising:

(a) contacting the basic waste with an acid to form modified basic waste and optionally insoluble salts of one or more target ions;

(b) contacting the modified basic waste with an electrolyzer to form (i) a product comprising insoluble salts of one or more target ions, or metallic deposition on the cathode of one or more target ions, and (ii) an acid; and

(c) optionally repeating step (a) at least once, wherein the acid of repeated step (a) comprises the acid from step (b)(ii).

[0061] Some embodiments provide a method of reducing chemical content in acidic waste comprising one or more target ions, the method comprising:

(a) contacting the acidic waste with a base to form modified acidic waste and optionally insoluble salts of one or more target ions;

(b) contacting the modified acidic waste with an electrolyzer to form (i) a base or a product comprising insoluble salts of one or more target ions, or metallic deposition on the cathode of one or more target ions, and (ii) an acid.

(c) optionally repeating step (a) at least once, wherein the base of repeated step (a) comprises the base of step (b)(i).

[0062] In some embodiments, the method further comprises separating the insoluble salts of one or more target ions of step (a) prior to performing step (b). In some embodiments, the separating comprises filtration. In some embodiments, the separating is filtration.

[0063] In some embodiments, step (c) is repeated at least once.

[0064] Some embodiments provide a method of reducing chemical content in basic waste comprising one or more target ions, the method comprising:

(a) contacting the basic waste with an acid to form (i) a first modified basic waste and optionally (ii) a first insoluble salts of one or more target ions;

(b) separating the first modified basic waste from the first insoluble salts of one or more target ions of step (a);

(c) contacting the first modified basic waste of step (a)(i) with base to form (i) insoluble metal hydroxides of one or more target ions; and (ii) a liquid rich in ions;

(d) contacting the liquid rich in ions of step (c)(ii) with an electrolyzer to form (i) a base, and (ii) an acid;

(e) optionally contacting the first insoluble salts of one or more target ions of step (a)(ii) with the acid from step (d)(ii) to form a (i) second insoluble salts of one or more target ions, and (ii) a second modified basic waste; wherein the products of step (e)(i) and (e)(ii) may be subjected to steps (b) – (d), wherein the base in repeated step (c) is from step (d)(i); and wherein

steps (b) – (e) may be repeated at least once.

[0065] In some embodiments, the method is performed continuously

[0066] Some embodiments provide a method of reducing chemical content in acidic waste comprising one or more target ions, the method comprising:

(a) contacting the acidic waste with a base and carbon dioxide to form (i) insoluble carbonate salts of one or more target ions; and (ii) a solution rich in ions;

(b) contacting the solution rich in ions of step (a)(ii) with an electrolyzer to regenerate (i) a base and (ii) an acid; and

(c) optionally repeating steps (a) and (b), wherein the base of repeated step (a) comprises the regenerated base of step (b)(i).

[0067] In some embodiments, the carbon dioxide is obtained from direct air capture (DAC). In some embodiments, the carbon dioxide is obtained from a waste stream.

[0068] In some embodiments, step (c) is repeated at least once.

[0069] Some embodiments provide a method of reducing chemical content in acidic waste comprising one or more target ions, the method comprising:

(a) contacting the acidic waste with an electrolyzer to form (i) an acid and (i) metal hydroxides or metallic deposition on the cathode of one or more target ions; and

(b) collecting the metal hydroxide or the metallic deposition of step (a).

[0070] In some embodiments, the electrolyzer is a single-membrane electrolyzer, two-membrane salt splitting electrolyzer, a multi-membrane salt-splitting electrolyzer, a chlor-alkali electrolyzer, a bipolar membrane electrodialysis electrolyzer, or a combination of any of the foregoing.

[0071] In some embodiments, a potential cutoff to the electrolysis is introduced to target a specific metallic deposition of one or more metals on the cathode.

[0072] In some embodiments, a potential cutoff to the electrolysis is introduced to selectively remove a target ion from the waste (i.e., to deposit one metal on the cathode) from a mixture of one or more target ions present in the waste (i.e., the catholyte). In some embodiments, the potential cutoff selectively removes ions of cobalt from the waste, providing cobalt metal. In some embodiments, the potential cutoff selectively removes ions of nickel from the waste, providing nickel metal.

[0073] In some embodiments, the methods disclosed herein can further comprise separating the basic product from the acid of step (b) prior to step (c).

[0074] In some embodiments, the methods disclosed herein can further comprise separating the acidic product from the base of step (b) prior to step (c).

[0075] In some embodiments, step (b) comprises sequentially contacting the acidic waste comprising one or more target ions with two or more independently selected bases. In some embodiments, the bases are the same. In some embodiments, the bases are different. In some embodiments, the bases each comprise an independently selected metal hydroxide.

[0076] In some embodiments, the carbon dioxide is provided as a composition, wherein the composition comprises carbon dioxide and at least one additional gas, as described herein. For example, some embodiments described herein utilize carbon dioxide, for example, to produce a metal carbonate or bicarbonate from a metal hydroxide. In some embodiments, the carbon dioxide composition comprises a concentrated carbon dioxide source (e.g., flue gas from, for example, a power station). In some embodiments, the carbon dioxide composition comprises a dilute carbon dioxide source (e.g., atmospheric carbon dioxide). In other words, some embodiments described herein comprise carbon dioxide removal and sequestration.

[0077] In some embodiments, the composition comprises carbon dioxide in an amount of

about 0.01 wt% to about 99.9 wt%, or about 0.01 wt% to about 1.5 wt%, or about 1 wt% to about 20 wt%, or about 5 wt% to about 20 wt%, or about 50 wt% to about 90 wt%. In some embodiments, the composition comprises carbon dioxide in an amount of about 0.01 wt% to about 99.9 wt%. In some embodiments, the composition comprises carbon dioxide in an amount of about 0.01 wt% to about 1.5 wt%. In some embodiments, the composition comprises carbon dioxide in an amount of about 1 wt% to about 10 wt%. In some embodiments, the composition comprises carbon dioxide in an amount of about 50 wt% to about 90 wt%.

[0078] In some embodiments, the carbonate salt and/or the bicarbonate salt is selected from sodium, potassium, lithium, and combinations of any of the foregoing. In some embodiments, the salt is sodium carbonate, potassium carbonate, lithium carbonate, or a combination of any of the foregoing. In some embodiments, the salt is sodium bicarbonate, potassium bicarbonate, lithium bicarbonate, or a combination of any of the foregoing.

[0079] In some embodiments, the methods disclosed herein further comprise sequential electrolysis. In some embodiments, the methods disclosed herein further comprise repeating each of steps (a)-(b) at least once using sequential electrolysis. In some embodiments, the methods disclosed herein further comprise repeating each of the contacting steps at least once using sequential electrolysis. In some embodiments, each of the steps comprising electrolysis are repeated using sequential electrolysis.

[0080] In some embodiments, the sequential electrolysis occurs via continuous multi-ion sequential electrowinning. In some embodiments, the sequential electrolysis comprises continuous multi-ion sequential electrowinning. In some embodiments, the sequential electrolysis is continuous multi-ion sequential electrowinning.

[0081] Some embodiments provide a method of reducing the environmental impact of acidic waste comprising one or more of mining drainage, mine tailings, manufacturing waste, industrial waste, agricultural runoff, and brine, the method comprising:

(a) contacting the acidic waste comprising one or more target ions with a base to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof;

(b) contacting the modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, with an electrolyzer to regenerate the base and form an acidic product comprising the one or more ions and optionally insoluble salts thereof, and

(c) repeating step (a) at least once, wherein the base of repeated step (a) comprises the base of step (b).

[0082] Some embodiments provide a method of reducing the environmental impact of

acidic waste, the method comprising:

contacting the acidic waste comprising one or more target ions with a base in an electrochemical cell to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, and the electrochemical cell regenerates the base and forms an acidic product comprising the one or more ions and optionally insoluble salts thereof;

wherein the electrochemical cell comprises an anode reservoir comprising an anode and the acid, and a cathode reservoir comprising a cathode and the base, wherein the anode reservoir and the cathode reservoir are separated by a separator.

[0083] Some embodiments provide a method of reducing the environmental impact of basic waste comprising one or more of mining drainage, mine tailings, manufacturing waste, industrial waste, agricultural runoff, and brine, the method comprising:

(a) contacting the basic waste comprising one or more target ions with an acid to form modified basic waste comprising the one or more ions and optionally insoluble salts thereof;

(b) contacting the modified basic waste comprising the one or more ions and optionally insoluble salts thereof, with an electrolyzer to regenerate the acid and form a basic product comprising the one or more ions and optionally insoluble salts thereof, and

(c) repeating step (a) at least once, wherein the acid of repeated step (a) comprises the acid from step (b).

[0084] Some embodiments provide a method of reducing the environmental impact of basic waste comprising one or more of mining drainage, mine tailings, manufacturing waste, industrial waste, agricultural runoff, and brine, the method comprising:

(a) contacting the basic waste comprising one or more target ions with an acid to form modified basic waste comprising the one or more ions and optionally insoluble salts thereof;

(b) contacting the modified basic waste comprising the one or more ions and optionally insoluble salts thereof, with an electrolyzer to regenerate the acid and form a basic product comprising the one or more ions and optionally insoluble salts thereof, and

(c) repeating step (a) at least once, wherein the acid of repeated step (a) comprises the acid from step (b).

[0085] Some embodiments provide a method of reducing chemical content in basic waste, the method comprising:

contacting the basic waste comprising one or more target ions with an acid in an electrochemical cell to form modified basic waste comprising the one or more ions and

optionally insoluble salts thereof, and the electrochemical cell regenerates the acid and forms a basic product comprising the one or more ions and optionally insoluble salts thereof;

wherein the electrochemical cell comprises an anode reservoir comprising an anode and the acid, and a cathode reservoir comprising a cathode and the base, wherein the anode reservoir and the cathode reservoir are separated by a separator.

[0086] Some embodiments provide a method of reducing chemical content in acidic waste, the method comprising:

contacting the acidic waste comprising one or more target ions with a base in an electrochemical cell to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, and the electrochemical cell regenerates the base and forms an acidic product comprising the one or more ions and optionally insoluble salts thereof;

wherein the electrochemical cell comprises an anode reservoir comprising an anode and the acid, and a cathode reservoir comprising a cathode and the base, wherein the anode reservoir and the cathode reservoir are separated by a separator.

[0087] Some embodiments provide a method of reducing sulfur, phosphorus, and/or organic content, wherein the organic content in basic waste, wherein the organic content comprises organic pollutants or contaminants (such as phenol derivatives), the method comprising:

(a) contacting the basic waste comprising one or more of sulfur, phosphorus, and/or organic content with an acid to form modified basic waste comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof;

(b) contacting the modified basic waste comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof, with an electrolyzer to form a basic product comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof, and regenerate the acid, and

(c) repeating step (a) at least once, wherein the acid of repeated step (a) comprises the acid from step (b).

[0088] Some embodiments provide a method of reducing one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof, wherein the organic content in acidic waste, wherein the organic content comprises organic pollutants or contaminants (such as phenol derivatives), the method comprising:

(a) contacting the acidic waste comprising one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof with a base to form modified acidic waste comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble

content thereof;

(b) contacting the modified acidic waste comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof, with an electrolyzer to regenerate the base and form an acidic product comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof, and

(c) repeating step (a) at least once, wherein the base of repeated step (a) comprises the base of step (b).

[0089] In some embodiments, the separator is an anion exchange membrane or a cation exchange membrane. In some embodiments, the separator is an anion exchange membrane. In some embodiments, the separator is a cation exchange membrane.

[0090] In some embodiments, the methods further comprise repeating the contacting at least once using sequential electrolysis.

[0091] In some embodiments, the sequential electrolysis occurs via continuous multi-ion sequential electrowinning. In some embodiments, the sequential electrolysis comprises continuous multi-ion sequential electrowinning. In some embodiments, the sequential electrolysis is continuous multi-ion sequential electrowinning.

[0092] In some embodiments, the methods further comprise separating the acidic product from the electrochemical cell.

[0093] In some embodiments, the methods further comprise further comprise separating the basic product from the electrochemical cell.

[0094] In some embodiments, the electrochemical cell is configured to reduce chemical content in basic waste.

[0095] In some embodiments, the electrochemical cell comprises:

an anode reservoir comprising an anode and an acid, and a cathode reservoir comprising a cathode and a base, wherein the anode reservoir and the cathode reservoir are separated by a separator;

a contactor configured to input the basic waste comprising one or more target ions into the anode reservoir, wherein the anode reservoir is configured to contact the basic waste with the acid to form modified basic waste comprising the one or more ions, and the cathode reservoir is configured to contact the modified basic waste comprising the one or more ions with the base to form a basic product comprising the one or more ions;

a first filtration system in contact with the anode reservoir configured to filter out any insoluble salts from the modified basic waste from the anode reservoir; and

a second filtration system in contact with the cathode reservoir configured to filter

out any insoluble salts from the basic product comprising the one or more ions and optionally insoluble salts thereof, from the cathode reservoir.

[0096] In some embodiments, the electrochemical cell is configured to reduce chemical content in acidic waste.

[0097] In some embodiments, the electrochemical cell is configured to reduce chemical content in acidic waste,

wherein the electrochemical cell comprises an anode reservoir comprising an anode and an acid, and a cathode reservoir comprising a cathode and a base, wherein the anode reservoir and the cathode reservoir are separated by a separator;

a contactor configured to input the acidic waste comprising one or more target ions into the cathode reservoir, wherein the cathode reservoir is configured to contact the acidic waste with the base to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, and the anode reservoir is configured to contact the modified acidic waste comprising the one or more ions with the acid to form an acidic product comprising the one or more ions and optionally insoluble salts thereof;

a first filtration system in contact with the cathode reservoir configured to filter out any insoluble salts from the modified acidic waste from the cathode reservoir; and

a second filtration system in contact with the anode reservoir configured to filter out any insoluble salts from the acidic product comprising the one or more ions and optionally insoluble salts thereof, from the anode reservoir.

[0098] In some embodiments, the acidic waste or basic waste is one or more of mining drainage, mine tailings, manufacturing waste, industrial waste, agricultural runoff, and brine.

[0099] In some embodiments, step (a) comprises sequentially contacting the acidic waste comprising the one or more ions with two or more independently selected bases.

[00100] In some embodiments, the method additionally comprises separating the insoluble salts or metallic deposition of step (b)(i) from the acid of step (b)(ii) prior to step (c).

[00101] In some embodiments, the base comprises a carbonate salt and/or a bicarbonate salt. In some embodiments, the carbonate salt and/or the bicarbonate salt is selected from sodium, potassium, lithium, and combinations of any of the foregoing.

Selected Systems

[00102] Some embodiments provide a system for reducing chemical content in acidic waste, comprising:

an electrochemical cell configured to reduce chemical content in acidic waste,

wherein the electrochemical cell comprises an anode reservoir comprising an anode and an acid, and a cathode reservoir comprising a cathode and a base, wherein the anode reservoir and the cathode reservoir are separated by a separator;

a contactor configured to input the acidic waste comprising one or more target ions into

a mixing reservoir, wherein the mixing reservoir is configured to contact the acidic waste in the mixing reservoir with the output from the cathode reservoir to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, and the anode reservoir is configured to contact the modified acidic waste in the mixing reservoir comprising the one or more ions with the acid to form an acidic product comprising the one or more ions and optionally insoluble salts thereof;

a first filtration system in contact with the mixing reservoir configured to filter out any insoluble salts from the modified acidic waste from the mixing reservoir; and

a second filtration system in contact with the anode reservoir configured to filter out any insoluble salts from the acidic product comprising the one or more ions and optionally insoluble salts thereof, from the anode reservoir.

[00103] Some embodiments provide a system for reducing chemical content in basic waste, comprising:

an electrochemical cell configured to reduce chemical content in basic waste, wherein the electrochemical cell comprises an anode reservoir comprising an anode and an acid, and a cathode reservoir comprising a cathode and a base, wherein the anode reservoir and the cathode reservoir are separated by a separator;

a contactor configured to input the basic waste comprising one or more target ions into a mixing reservoir, wherein the mixing reservoir is configured to contact the basic waste comprising one or more target ions with the output from the anode reservoir to form modified basic waste comprising the one or more ions and optionally insoluble salts thereof, and the cathode reservoir is configured to contact the modified basic waste in the mixing reservoir comprising the one or more ions with the base to form a basic product comprising the one or more ions and optionally insoluble salts thereof;

a first filtration system in contact with the mixing reservoir configured to filter out any insoluble salts from the modified basic waste from the mixing reservoir; and

a second filtration system in contact with the cathode reservoir configured to filter out any insoluble salts from the basic product comprising the one or more ions and optionally

insoluble salts thereof, from the cathode reservoir.

[00104] Some embodiments provide a system for reducing sulfur, phosphorus, and/or organic content in basic waste, wherein the organic content comprises organic pollutants or contaminants (such as phenol derivatives), the system comprising:

- an electrochemical cell configured to reduce sulfur, phosphorus, and/or organic content in basic waste, wherein the electrochemical cell comprises an anode reservoir comprising an anode and an acid, and a cathode reservoir comprising a cathode and a base, wherein the anode reservoir and the cathode reservoir are separated by a separator;

- a contactor configured to input the basic waste comprising sulfur, phosphorus, and/or organic content into a mixing reservoir, wherein the mixing reservoir is configured to contact the basic waste comprising sulfur, phosphorus, and/or organic content with the output from the anode reservoir to form modified basic waste comprising the sulfur, phosphorus, and/or organic content, and the cathode reservoir is configured to contact the modified basic waste in the mixing reservoir comprising the sulfur, phosphorus, and/or organic content with the base to form a basic product comprising the sulfur, phosphorus, and/or organic content and optionally insoluble salts thereof;

- a first filtration system in contact with the mixing reservoir configured to filter out any insoluble salts from the modified basic waste from the mixing reservoir; and

- a second filtration system in contact with the cathode reservoir configured to filter out any insoluble salts from the basic product comprising the one or more ions and optionally insoluble salts thereof, from the cathode reservoir.

[00105] Some embodiments provide a system for reducing one or more of sulfur, phosphorus, and/or organic content and/or insoluble content in acidic waste, wherein the organic content comprises organic pollutants or contaminants (such as phenol derivatives), the system comprising:

- an electrochemical cell configured to reduce sulfur, phosphorus, and/or organic content in acidic waste, wherein the electrochemical cell comprises an anode reservoir comprising an anode and an acid, and a cathode reservoir comprising a cathode and a base, wherein the anode reservoir and the cathode reservoir are separated by a separator;

- an electrochemical cell configured to reduce sulfur, phosphorus, and/or organic content and/or insoluble content in acidic waste, wherein the electrochemical cell comprises an anode reservoir comprising an anode and an acid, and a cathode reservoir comprising a cathode and a base, wherein the anode reservoir and the cathode reservoir are separated by a separator;

- a contactor configured to input the acidic waste comprising sulfur, phosphorus,

and/or organic content and/or insoluble content into a mixing reservoir, wherein the mixing reservoir is configured to contact the acidic waste in the mixing reservoir with the output from the cathode reservoir to form modified acidic waste comprising the sulfur, phosphorus, and/or organic content and/or insoluble content and optionally insoluble salts thereof, and the anode reservoir is configured to contact the modified acidic waste in the mixing reservoir comprising the sulfur, phosphorus, and/or organic content and/or insoluble content with the acid to form an acidic product comprising the sulfur, phosphorus, and/or organic content and/or insoluble content and optionally insoluble salts thereof;

a first filtration system in contact with the mixing reservoir configured to filter out any insoluble salts from the modified acidic waste from the mixing reservoir; and

a second filtration system in contact with the anode reservoir configured to filter out any insoluble salts from the acidic product comprising the one or more ions and optionally insoluble salts thereof, from the anode reservoir.

[00106] In some embodiments, the systems described herein regenerate an acid. In some embodiments, the systems described herein regenerate a base. In some embodiments, the systems described herein are configured to reuse the regenerated acid and/or the regenerated base.

[00107] In some embodiments, the separator is an anion exchange membrane or a cation exchange membrane. In some embodiments, the separator is an anion exchange membrane. In some embodiments, the separator is a cation exchange membrane.

[00108] In some embodiments, the base is selected from the group consisting of NaOH, LiOH, KOH, Na₂CO₃, and NaHCO₃, or any combination thereof. In some embodiments, the base is NaOH.

[00109] In some embodiments, the acid is selected from the group consisting of HCl, HNO₃, H₂SO₄, and H₃PO₄ or any combination thereof. In some embodiments, the acid is HCl or HNO₃, or any combination thereof.

[00110] In some embodiments, the one or more target ions are metallic ions selected from ions of lithium, sodium, potassium, beryllium, magnesium, calcium, strontium, barium, radium, aluminum, gallium, indium, tin, thallium, lead, bismuth, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, and mercury.

[00111] In some embodiments, the one or more target ions are metallic ions selected from ions of strontium, barium, radium, aluminum, gallium, indium, tin, thallium, lead, scandium,

titanium, vanadium, chromium, manganese, iron, cobalt, nickel, zinc, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, cadmium, tantalum, rhenium, osmium, and iridium.

[00112] In some embodiments, the one or more target ions are metallic ions selected from ions of bismuth, copper, silver, tungsten, platinum, gold, and mercury.

[00113] In some embodiments, the one or more target ions are metallic ions selected from ions of nickel and cobalt.

[00114] In some embodiments, the one or more target ions are metallic ions selected from ions of tin, lead, iron, cobalt, nickel, copper, zinc, palladium, silver, cadmium, platinum, and gold.

[00115] In some embodiments, the methods described herein are used to remove metallic ions of nickel, cobalt, lead, and/or cadmium from acidic mine waste, thereby reducing detrimental environmental impact of such waste.

[00116] In some embodiments, performance of the methods and operation of the systems described herein is carbon neutral.

[00117] The methods disclosed herein can include (a) contacting acidic waste or basic waste comprising calcium and/or magnesium ions with an acid for basic waste or a base for acidic waste to form modified waste comprising calcium and/or magnesium ions and optionally insoluble salts thereof; (b) contacting the modified waste with an electrolyzer to form a basic product comprising the calcium and/or magnesium ions and optionally insoluble salts thereof, and regenerate the acid for the basic waste, or to form an acidic product comprising the calcium and/or magnesium ions and optionally insoluble salts thereof, and regenerate the base for the acidic waste. In some embodiments, the methods can include a step (d), wherein step (d) includes repeating each of steps (a)-(b) at least once, wherein the acid of repeated step (a) comprises the acid or the base from step (c).

[00118] The methods disclosed herein can include (a) contacting acidic waste or basic waste comprising calcium and/or magnesium ions with an acid for basic waste or a base for acidic waste to form modified waste comprising calcium and/or magnesium ions and optionally insoluble salts thereof; (b) contacting the modified waste with a base and carbon dioxide to produce calcium carbonate, and/or insoluble salts thereof, and a calcium and/or magnesium-deficient liquid; and (c) contacting the calcium and/or magnesium-deficient liquid with an electrolyzer to regenerate the acid and the base.

[00119] The methods disclosed herein can include (a) contacting the acidic waste comprising one or more calcium and/or magnesium ions with a base and carbon dioxide to

form modified acidic waste comprising the one or more calcium and/or magnesium carbonates, and/or insoluble salts thereof, from the one or more calcium and/or magnesium ions; and (b) contacting the modified acidic waste comprising the one or more calcium and/or magnesium carbonates, and/or insoluble salts thereof, with an electrolyzer to regenerate the base and form an acidic product comprising the one or more calcium and/or magnesium carbonates, and/or insoluble salts thereof.

[00120] The methods disclosed herein can include contacting the basic waste comprising one or more calcium and/or magnesium ions with an acid in an electrochemical cell to form modified basic waste comprising the one or more calcium and/or magnesium ions and optionally insoluble salts thereof, and the electrochemical cell regenerates the acid and forms a basic product comprising one or more calcium and/or magnesium ions and optionally insoluble salts thereof; wherein the electrochemical cell comprises an anode reservoir comprising an anode and the acid, and a cathode reservoir comprising a cathode and the base, wherein the anode reservoir and the cathode reservoir are separated by a separator.

[00121] The methods disclosed herein can include contacting the acidic waste comprising one or more calcium and/or magnesium ions with a base in an electrochemical cell to form modified acidic waste comprising the one or more calcium and/or magnesium ions and optionally insoluble salts thereof, and the electrochemical cell regenerates the base and forms an acidic product comprising the one or more calcium and/or magnesium ions and optionally insoluble salts thereof; wherein the electrochemical cell comprises an anode reservoir comprising an anode and the acid, and a cathode reservoir comprising a cathode and the base, wherein the anode reservoir and the cathode reservoir are separated by a separator.

[00122] The methods disclosed herein can include reducing the environmental impact of acidic waste containing the one or more ions. In some embodiments, the one or more ions include one or more calcium and/or magnesium ions.

[00123] The methods disclosed herein can include reducing the environmental impact of basic waste containing the one or more ions. In some embodiments, the one or more ions include one or more calcium and/or magnesium ions.

[00124] Some embodiments provide a system comprising the electrochemical cell as disclosed herein.

[00125] In some embodiments, the system is configured to reduce chemical content in basic waste or acidic waste.

[00126] In some embodiments, the system can include an electrochemical cell configured to reduce chemical content in basic waste or acidic waste, wherein the electrochemical cell

comprises an anode reservoir comprising an anode and an acid, and a cathode reservoir comprising a cathode and a base, wherein the anode reservoir and the cathode reservoir are separated by a separator; and a contactor. The contactor can be configured to input the basic waste comprising one or more target ions into the cathode reservoir, wherein the cathode reservoir is configured to contact the acidic waste with the base to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, and the anode reservoir is configured to contact the modified acidic waste comprising the one or more ions with the acid to form an acidic product comprising the one or more ions and optionally insoluble salts thereof; the contactor can be configured to input the basic waste comprising one or more target ions into the anode reservoir, wherein the anode reservoir is configured to contact the basic waste with the acid to form modified basic waste comprising the one or more ions and optionally insoluble salts thereof, and the cathode reservoir is configured to contact the modified basic waste comprising the one or more ions with the base to form a basic product comprising the one or more ions and optionally insoluble salts thereof.

[00127] In some embodiments, the system includes a first filtration system in contact with the anode reservoir configured to filter out any insoluble salts from the modified waste from the anode reservoir.

[00128] In some embodiments, the system includes a second filtration system in contact with the cathode reservoir configured to filter out any insoluble salts from the basic product comprising the one or more ions and optionally insoluble salts thereof, from the cathode reservoir.

[00129] In some embodiments, the system includes a first filtration system in contact with the cathode reservoir configured to filter the modified waste from the cathode reservoir.

[00130] In some embodiments, the system includes a second filtration system in contact with the anode reservoir configured to filter the acidic product comprising the one or more ions and optionally insoluble salts thereof, from the anode reservoir.

[00131] In some embodiments, the system further comprises a tube connecting from the anode reservoir to the cathode reservoir configured to output hydrogen gas from the cathode reservoir and input hydrogen gas into the anode reservoir.

[00132] In some embodiments, the system further comprises a conducting material connecting the anode to the cathode configured to output electrons from the anode and input the electrons to the cathode.

[00133] In some embodiments, the system further comprises a valve configured to input water into the anode reservoir.

[00134] In some embodiments, waste comprises calcium oxide. In some embodiments, waste comprises calcium hydroxide.

[00135] In some embodiments, waste further comprises one or more additional materials including, but not limited to, silicates, silicon dioxide, iron oxide, aluminum oxide, aluminates (e.g., tricalcium aluminate), and other minerals.

[00136] Applicable acids, bases, and salts, include but are not limited to, HCl, NaOH, NaCl and $\text{Ca}(\text{OH})_2$. In some embodiments, the base comprises a carbonate salt and/or a bicarbonate salt. In some embodiments, the carbonate salt and/or the bicarbonate salt is selected from sodium, potassium, lithium, and combinations of any of the foregoing.

[00137] Acid Treatment: The waste is subject to reaction with an acid under controlled temperature and stirring. After acid treatment, the modified waste can be filtered. The precipitates can then be washed and subject to sieving. A variety of acids, including but not limited to H_2SO_4 , HCl, HNO_3 , HBr, HI, acetic acid, H_3PO_4 , formic acid, maleic acid, can be used in the acid treatment step for the methods disclosed herein. The concentration of the acids can vary from 0.05 M to 30 M. Any type of stirring/agitation methods may be applied to ensure sufficient reaction. *In situ* sensing, including but not limited to pH, conductivity, atomic absorption spectroscopy, NMR spectroscopy, ICP-OES, can be implemented in this step and allow real-time monitoring of reaction progress and feedback control.

[00138] Base Treatment: The waste can be mixed with a base (e.g., a base solution). The waste can include a calcium salt (e.g., one or more of CaCl_2 , CaSO_4 , and $\text{Ca}(\text{NO}_3)_2$) and one or more of MgCl_2 , FeCl_2 , FeCl_3 , MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, and $\text{Mg}(\text{NO}_3)_2$. In some embodiments, the waste reacts and turns to calcium and/or magnesium precipitate (e.g., calcium hydroxide and/or magnesium hydroxide), including but not limited to $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, which precipitates out from solution. The calcium and/or magnesium precipitate (e.g., metal hydroxides) are filtered out of the solution. It has been discovered that different metal hydroxides can precipitate out at different pH. Therefore, implementing *in situ* sensing can allow better monitoring of reaction progress and enable easier separation of different products. Just like the acid treatment step, a large variety of bases, at different concentrations, may be implemented in this step.

[00139] Electrolysis: The waste (e.g., modified waste) after the acid and/or base treatment, has high salt concentration (such as one or more of LiCl, NaCl, KCl, Li_2SO_4 , Na_2SO_4 , K_2SO_4 , LiNO_3 , NaNO_3 , and KNO_3). The waste is fed into an electrolyzer to generate the acid and/or base, used in previous steps, respectively. Several cell structures and electrolysis strategies can be implemented here. Some examples are explained below.

[00140] A two-membrane salt-splitting cell can be used in the methods disclosed herein, with water oxidation, i.e. $\text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$, on the anode side and water reduction, i.e. $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$, on the cathode side. The electrolyzer can include an anion exchange membrane (AEM) and a cation exchange membrane (CEM). In some embodiments, the AEM and CEM can be replaced with a bipolar membrane. The waste can be fed into a central reservoir that can be connected to the anode and cathode compartments. When a large enough voltage is applied to the electrodes, a water splitting reaction takes place. At the anode, water is oxidized to oxygen, and the anions are pulled from the central reservoir, which results in an acid solution in the anode electrolyte. Meanwhile at the cathode, water is reduced to hydrogen, and cations are pulled from the central reservoir, creating a base electrolyte in the cathode reservoir. The thermodynamic voltage for the reaction is 1.23 V. In addition, a possible auxiliary device to this setup is a $\text{H}_2 + \text{O}_2$ fuel cell, which can cover part of the electricity cost.

[00141] A slightly modified version of the two-membrane salt splitting cell can be used in the methods disclosed herein. Instead of reduction of water on the cathode side, oxygen reduction, i.e. $1/2\text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$, is utilized, and the O_2 gas is circulated in between anode and cathode side. There is a smaller voltage difference between anode and cathode (0 V to ~ 0.8 V depending on the pH gradient), which can lead to less energetic cost during electrolysis.

[00142] An additional electrolyzer can be used in the methods disclosed herein. Instead of oxidation of water on the anode side, hydrogen oxidation, i.e. $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$, is utilized. Hydrogen is circulated internally. There is a smaller voltage difference between anode and cathode which can lead to less energetic cost during electrolysis.

[00143] Another possible electrolyzer that can be used in the methods disclosed herein is a classic chlor-alkali electrolyzer. A cation membrane separates the anode side from the cathode side. During electrolysis, chloride ions are oxidized to chlorine, i.e. $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$, at the anode, and water is reduced to hydrogen at the cathode. A fuel cell is required to convert hydrogen and chlorine into HCl gas.

[00144] Further, a bipolar membrane electrodialysis cell can be used in the methods disclosed herein.

[00145] An additional method for reducing chemical content in waste is disclosed herein. The method is similar to the methods disclosed above except for the addition of CO_2 -rich gas, such as flue gas or air, into the base treatment reservoir, thereby converting the one or more metal ions to carbonates (e.g., $\text{Ca}(\text{OH})_2$ to CaCO_3). This is to combine carbon capture and sequestration with reducing chemical content in waste. In addition, because of the low

solubility of CaCO_3 in water, separation and purification of CaCO_3 from the calcium-deficient liquid is much easier compared to Ca(OH)_2 . The same idea applies to other metal hydroxides, such as Mg(OH)_2 , Fe(OH)_2 , etc., and carbonates, e.g., but not limited to, MgCO_3 , FeCO_3 , $\text{Fe}_2(\text{CO}_3)_3$, etc. By sensing the CO_2 concentration and flow rate at the inlet and exit, one can monitor CO_2 capture in real time.

[00146] An additional method for reducing chemical content in waste is disclosed herein. The base stream coming off from the electrolyzer is exposed to CO_2 rich gas, such as flue gas or air, on a contactor, and is converted to aqueous carbonates, such as, but not limited to, Na_2CO_3 , NaHCO_3 , K_2CO_3 , and KHCO_3 . The aqueous base stream has higher basicity and concentration of active material compared to the semi-soluble base used in the methods disclosed herein. Therefore, the CO_2 capture rate is expected to be faster and CO_2 can be extracted from low concentration streams such as air. The aqueous carbonate stream reacts with the product of acid stream to form carbonate precipitates such as, but not limited to, CaCO_3 , MgCO_3 , $\text{Fe}_2(\text{CO}_3)_3$, or $\text{Al}_2(\text{CO}_3)_3$. Different carbonate products will precipitate out at different pH, thus it is possible to obtain pure products through carefully controlling the titration process.

[00147] An additional method for reducing chemical content in waste is disclosed herein. In this approach, the filtrate from the acid treatment is subject to direct electrolysis. Semi-soluble hydroxides are formed in the cathode side of the electrolyzer and can be separated/purified for sale. This way, fewer steps are involved, so fewer reactors are needed. In addition, only one membrane is needed in the electrolyzer, which can decrease costs. Several electrolyzers can be used in the methods disclosed herein. This design employs water oxidation at the anode and water reduction at the cathode. Only an AEM is used to separate two reservoirs. Chloride is allowed to pass from the cathode side to the anode side during electrolysis. The filtrate from the acid treatment, containing CaCl_2 or other soluble salts, is passed into the cathode side, and the resulting solution will contain high hydroxide content, both dissolved in water and in a slurry. To increase conductivity, a small amount, from 0.01 M to 1 M, of salt such as NaCl or KCl can be added to the anode side. The second design that is the same design as the first except this design uses oxygen reduction for the cathode. The third design that is the same design as the first design except this design uses hydrogen oxidation for the anode.

[00148] An additional method for reducing chemical content in waste is disclosed herein. In this approach, all the separated steps described in the original approach are combined together. The neutralization of the waste takes place in the anode reservoir or cathode reservoir of the electrolysis cell and, in some cases, the hydroxide precipitation step takes place in the cathode side of the cell. This system requires the least equipment, hence lower capital expenditures to

realize. In addition, as soon as acid is generated at the anode, it is consumed by $\text{Ca}(\text{OH})_2$. The hydroxide generated at the cathode reacts with CaCl_2 and form precipitates. Therefore, the pH gradient across the AEM will be small. This is beneficial because undesired ion leakage will be small and the concentration overpotential will also be small, leading to a lower energy cost. The hydroxides can include, but are not limited to, calcium hydroxide, magnesium hydroxide, aluminum hydroxide, iron hydroxide (both iron(II) and iron(III)).

[00149] Two chamber single AEM membrane electrolyzers have a component cost and complexity advantage over multi membrane systems, but pose some unique challenges in scaling up. Namely, this configuration separates products in time rather than in spaces compared to the 2 membrane 3 chamber electrolyzers. To deal with this particularity, it is found that a batch wise system and a continuous system, can be useful. In the batch configuration, continuous processing would be achieved by a series of settling tank electrolyzer pairs connected by circulation pumps. In this configuration a given tank would be charged and the solution circulates through the electrolyzer to allow the desired hydroxides to precipitate out of solution and be collected in the connected settling tank. Continuous production can be achieved by staggered charging and processing of several of these pairs.

[00150] In the continuous system (e.g., continuous multi-ion sequential electrowinning via sequential electrolysis or continuous base treatment), several combined electrolyzer settling tank pairs would be combined in series. Different voltages are applied to each electrolyzer unit in order to precipitate out different hydroxide species at lower power consumption. The solution to be processed would flow slowly from one cell to the next producing a gradient of pH and precipitation products going down the line.

[00151] In some embodiments, the waste (as described herein) comprising one or more ions contains the one or more ions at a concentration of about 0.0001M to about 5M, about 0.001M to about 0.5M, about 0.001M to about 0.1M, about 0.001M to about 0.01M, about 0.01M to about 0.10M, about 0.05M to about 0.25M, about 0.10M to about 0.5M, about 0.25M to about 0.75M, about 0.5M to about 1.0M, or any value in between.

[00152] In some embodiments, the one or more ions will reduce at the cathode resulting in the one or more metals to deposit (plate) onto the cathode.

[00153] In some embodiments, the one or more ions are comprised of salt pairs and/or complexes with sulfur, phosphorus, and/or organic containing ions.

[00154] Some embodiments provide a method of reducing sulfur, phosphorus, and/or organic content, wherein the organic content includes organic pollutants or contaminants such as phenol derivatives in basic waste, the method comprising:

(a) contacting the basic waste comprising one or more of sulfur, phosphorus, and/or organic content with an acid to form modified basic waste comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof;

(b) contacting the modified basic waste comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof, with an electrolyzer to form a basic product comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof, and regenerate the acid, and

(c) repeating step (a) at least once, wherein the acid of repeated step (a) comprises the acid from step (b).

[00155] Some embodiments provide a method of reducing one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof, wherein the organic content includes organic pollutants or contaminants such as phenol derivatives in acidic waste, the method comprising:

(a) contacting the acidic waste comprising one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof with a base to form modified acidic waste comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof;

(b) contacting the modified acidic waste comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof, with an electrolyzer to regenerate the base and form an acidic product comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof; and

(c) repeating step (a) at least once, wherein the base of repeated step (a) comprises the base of step (b).

[00156] Some embodiments provide a method of reducing one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof in basic waste, the method comprising:

contacting the basic waste comprising one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof with an acid in an electrochemical cell to form modified basic waste comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof, and the electrochemical cell regenerates the acid and forms a basic product comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof;

wherein the electrochemical cell comprises an anode reservoir comprising an anode and the acid, and a cathode reservoir comprising a cathode and the base, wherein the anode reservoir

and the cathode reservoir are separated by a separator.

[00157] Some embodiments provide a method of reducing one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof in acidic waste, the method comprising:

contacting the acidic waste comprising one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof with a base in an electrochemical cell to form modified basic waste comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof, and the electrochemical cell regenerates the base and forms an acidic product comprising the one or more of sulfur, phosphorus, and/or organic content and/or insoluble content thereof;

wherein the electrochemical cell comprises an anode reservoir comprising an anode and the acid, and a cathode reservoir comprising a cathode and the base, wherein the anode reservoir and the cathode reservoir are separated by a separator.

[00158] In some embodiments, the one or more one or more of sulfur, phosphorus, and/or organic content is sulfur content, e.g., sulfates, sulfites, metal sulfides, or hydrogen sulfide.

[00159] In some embodiments, the one or more one or more of sulfur, phosphorus, and/or organic content is phosphorus content, e.g., polyphosphate or phosphate salts.

[00160] In some embodiments, the one or more one or more of sulfur, phosphorus, and/or organic content is organic content, e.g., phenol derivatives.

[00161] In some embodiments, the waste (as described herein) comprising one or more of sulfur, phosphorus, and/or organic content contains the one or more of sulfur, phosphorus, and/or organic content at a concentration of about 0.0001M to about 5M, about 0.001M to about 0.5M, about 0.001M to about 0.1M, about 0.001M to about 0.01M, about 0.01M to about 0.10M, about 0.05M to about 0.25M, about 0.10M to about 0.5M, about 0.25M to about 0.75M, about 0.5M to about 1.0M, or any value in between.

[00162] Some embodiments provide a mobile apparatus for performing the methods described herein, for example, an apparatus that is configured to be moveable and/or is attached to a mechanism for moving the apparatus from location to location.

[00163] For example, an additional aspect of this disclosure provides a mobile processing plant for removing chemical content from waste (such as mine drainage), comprising:

a mobile electrochemical cell configured to reduce chemical content in waste, wherein the electrochemical cell comprises an anode reservoir comprising an anode and an acid, and a cathode reservoir comprising a cathode and a base, wherein the anode reservoir

and the cathode reservoir are separated by a separator; or

a contactor configured to input the waste into the electrochemical cell;

a filtration system in contact with the anode reservoir; and

a filtration system in contact with the cathode reservoir.

[00164] In some embodiments, the mobile processing plant is comprised of a railroad car, which is transported by rail to the site where the waste is accessible. In some embodiments, the mobile processing plant is comprised of a trailer, which is transported by road to the site where the waste is accessible. In some embodiments, the mobile processing plant is comprised of a truck, which travels by road to the site where the waste is accessible. In some embodiments, the mobile processing plant is comprised of a barge, which is transported by water to the site where the waste is accessible. In some embodiments, the mobile processing plant is comprised of a ship which travels by water to the site where the waste is accessible. In some embodiments, the mobile processing plant is comprised of an aircraft which travels by air to the site where the waste is accessible.

[00165] Some embodiments provide a system substantially as shown in FIG. 1 configured to perform the methods described herein.

[00166] Some embodiments provide a system substantially as shown in FIG. 2 configured to perform the methods described herein.

[00167] Some embodiments provide a system substantially as shown in FIG. 4 configured to perform the methods described herein.

[00168] Some embodiments provide a system substantially as shown in FIG. 5 configured to perform the methods described herein.

[00169] Some embodiments provide a system substantially as shown in FIG. 6A configured to perform the methods described herein.

EXAMPLES

Materials and methods

[00170] The Scanning electron microscopy was performed on SNE-4500M Plus using the following protocol:

[00171] Instrument Preparation: Power on the SEM; Open the Nanoeye software; vacuum the chamber; release the vacuum;

[00172] Sample Preparation: Cut the cathode after reaction to an appropriate size; Attach the cathode sample to the sample mount using a double-sided carbon tape; Measure the width and height of the sample mount, and enter the sample information into the software;

[00173] Load the Sample Mount: remove and load sample chamber; calibrate the sample stage by clicking the 'calibrate' button in the software; Insert sample chamber to the first stopping notch and take a picture of the sample; Fully insert sample chamber; exchange again;

[00174] Scan: set accelerating voltage: 10 kV; detector: SE, vacuum: high; start, and watch the emission current, should be around 100 μ A; Adjust the spot size accordingly; select area of interest; adjust accordingly with coarse and fine controls; Adjust contrast and brightness; capture fine image.

[00175] Energy-dispersive X-ray spectroscopy (EDS) was performed with EDS instrument using ESPRIT software and using the following protocol:

[00176] Adjust the spot size with live scan; Power on the EDS; Open the ESPRIT software; The count should be above 10; capture scan; select area of interest; then acquire spectrum; open the element map and select elements of interest and quantify and save to the report.

Example 1. Basic mine drainage treatment procedures 1 and 2

[00177] Described herein are two selected procedures for removing metallic content from red mud waste.

[00178] Red mud, i.e., or bauxite mine tailings is usually highly basic (pH 10-13) and is a slurry of chemical compositions, including: Fe_2O_3 (Iron Oxide): 5-60%; Al_2O_3 (Aluminum Oxide): 5-30%; TiO_2 (Titanium Dioxide): 0-15%; CaO (Calcium Oxide): 2-14%; SiO_2 (Silicon Dioxide): 3-50%; and Na_2O (Sodium Oxide): 1-10%.

[00179] In procedure 1 (FIG. 1), the pH of the mine tailings is decreased by addition of acid generated from an electrolyzer to target specific metallic content. For example, adjusting the pH to about 9 followed by filtration provides a solid containing metallic content and/or other insoluble material and a pH 9 filtrate comprising calcium and/or magnesium salts. The pH 9 filtrate may be contacted with an electrolyzer, to obtain a precipitate comprising $\text{Ca}(\text{OH})_2$ and/or $\text{Mg}(\text{OH})_2$ and acid. The $\text{Ca}(\text{OH})_2$ and/or $\text{Mg}(\text{OH})_2$ may be valorized (e.g., as concrete precursors), and the acid may be subsequently used in the process.

[00180] In a second stage, the solid containing metallic content and/or other insoluble material from the initial pH 9 treatment is contacted with acid to achieve a pH of about 6 followed by filtration to provide a solid containing metallic content and/or other insoluble material and a pH 6 filtrate comprising aluminum and/or copper salts. The pH 6 filtrate may be contacted with an electrolyzer to obtain a precipitate comprising $\text{Al}(\text{OH})_3$ and/or $\text{Cu}(\text{OH})_2$ and acid. The $\text{Al}(\text{OH})_3$ may be valorized and the acid may be subsequently used in the process.

[00181] In a third stage, the solid containing metallic content and/or other insoluble material

from the pH 6 treatment is contacted with acid to achieve a pH of about 1 followed by filtration to provide a solid containing metallic content, e.g., sodium silicates (silica), and/or other insoluble material and a pH 1 filtrate comprising ferrous and/or ferric salts. The pH 1 filtrate may be contacted with an electrolyzer, to obtain a precipitate comprising $\text{Fe}(\text{OH})_3$ and/or $\text{Fe}(\text{OH})_2$ and/or metallic Fe, and acid. Upon filtration, the $\text{Fe}(\text{OH})_3$ and/or $\text{Fe}(\text{OH})_2$ and/or metallic Fe can be valorized, and the acid subsequently used in the process.

[00182] In procedure 2 (FIG. 2), the pH of the mine tailings is decreased by addition of acid generated from an electrolyzer to target specific metallic content. For example, adjusting the pH to about 9 followed by filtration provides a solid containing metallic content and/or other insoluble material and a pH 9 filtrate. The pH 9 filtrate may be treated with base, e.g., NaOH, generated from an electrolyzer, to obtain a precipitate comprising $\text{Ca}(\text{OH})_2$ and/or $\text{Mg}(\text{OH})_2$ and a liquid rich in ions, for example Na^+ , K^+ , Cl^- , and various anions of nitrogen, sulfur, and phosphorus. Filtration of this mixture provides $\text{Ca}(\text{OH})_2$ and/or $\text{Mg}(\text{OH})_2$, which can be valorized (e.g., as concrete precursors), and filtrate rich in ions. The filtrate rich in ions can be subjected to electrodialysis or an electrolyzer to generate acid and base solutions to be subsequently used in the process.

[00183] In a second stage, the solid containing metallic content and/or other insoluble material from the initial pH 9 treatment is contacted with acid to achieve a pH of about 6 followed by filtration to provide a solid containing metallic content and/or other insoluble material and a pH 6 filtrate. The pH 6 filtrate may be treated with base, e.g., NaOH, generated from an electrolyzer, to obtain a precipitate comprising $\text{Al}(\text{OH})_3$ and a liquid rich in ions. Upon filtration, the filtrate rich in ions can be subjected to electrodialysis or an electrolyzer to generate acid and base solutions to be subsequently used in the process, and the $\text{Al}(\text{OH})_3$ may be valorized.

[00184] In a third stage, the solid containing metallic content and/or other insoluble material from the pH 6 treatment is contacted with acid to achieve a pH of about 1 followed by filtration to provide a solid containing metallic content, e.g., sodium silicates (silica), and/or other insoluble material and a pH 1 filtrate. The pH 1 filtrate may be treated with base, e.g., NaOH, generated from an electrolyzer, to obtain a precipitate comprising $\text{Fe}(\text{OH})_3$ and/or $\text{Fe}(\text{OH})_2$ and a liquid rich in ions. Upon filtration, the filtrate rich in ions can be subjected to electrodialysis or an electrolyzer to generate acid and base solutions to be subsequently used in the process, and the precipitate comprising $\text{Fe}(\text{OH})_3$ and/or $\text{Fe}(\text{OH})_2$ can be valorized.

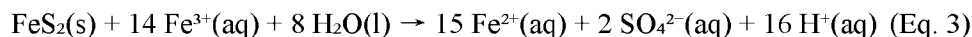
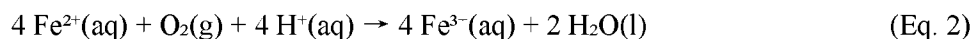
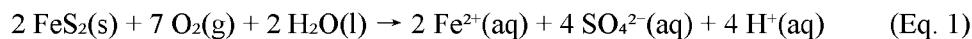
[00185] As described in the above two procedures, the pH of the mine tailings is adjusted by adding acid. Different cationic species will dissolve, a.k.a. leached, at different pH and can

be separated from the rest through filtration. The liquid containing a dissolved salt is then subjected to electrolysis (procedure 1) or mixing with NaOH (procedure 2) to form metal plates in the cathode (in the case of iron only) or metal hydroxides. These metal hydroxides and metal plates can be further refined before sale. The acid used in the pH adjustment steps is generated as a byproduct of electrolysis or electrodialysis of salts, e.g., NaCl, NaNO₃, or Na₂SO₄. After the treatment, the initial slurry of mixed metal hydroxides is converted to separated metal hydroxides or metal plates, which are of much higher value. The residual liquid will contain much lower concentrations of heavy metals, hence safer to discharge.

Example 2. Acidic mine drainage treatment procedures 3 and 4

[00186] Acid mine drainage is the outflow of acidic, metal-laden water from mines and similar disturbed sites. It occurs naturally but is worsened by mining and construction activities, especially in areas with sulfide-rich rocks. The resulting acidic water can contain toxic metals (FIG. 3), harming aquatic life. Similar issues arise from disturbed acid sulfate soils formed in coastal areas.

[00187] Mine tailings that contains lots of metal sulfide may spontaneously convert to acid drainage through the following reactions:



[00188] It should be noted that nickel, cobalt, copper, zinc and other metals may lead to the same reactions and cause acid build-up.

[00189] Current treatment methods involve neutralization with calcium oxide, calcium carbonate or calcium silicate and ion exchange.

[00190] Described herein are two selected procedures for removing metallic content from acidic mine drainage.

[00191] In procedure 3 (FIG. 4), the pH of the acidic drainage, which may contain insoluble silica salts, is filtered prior to contacting with an electrolyzer. The obtained solids, e.g., silica/sand may be sold or otherwise re-purposed. The filtrate may be contacted with an electrolyzer to obtain acid and metal hydroxides or metal plated onto the cathode. The metal hydroxides or metal plates may be further refined before sale. The acid generated in the electrolyzer may be sold directly, refine, or used for refining metal and/or metal hydroxides.

[00192] In procedure 4 (FIG. 5), the pH of the acidic drainage is adjusted to target specific

metallic content. For example, increasing the pH to about 3 followed by filtration provides a solid comprised of $\text{Fe}(\text{OH})_3$ and a pH 3 filtrate rich in metal and non-metal ions. The $\text{Fe}(\text{OH})_3$ may be further refined prior to sale.

[00193] In a second stage, the pH 3 filtrate rich in metal and non-metal ions may be treated with base generated from an electrolyzer, to a pH of about 8 to obtain a precipitate comprising $\text{Al}(\text{OH})_3$ and/or $\text{Cu}(\text{OH})_2$ and a liquid rich in metal and non-metal ions. Filtration of this mixture provides a pH 8 filtrate rich in metal and non-metal ions and solid $\text{Al}(\text{OH})_3$ and/or $\text{Cu}(\text{OH})_2$, which can be further refined prior to sale.

[00194] In a third step, the pH 8 filtrate rich in metal and non-metal ions can be treated with base generated from an electrolyzer to a pH of about 12 to obtain a precipitate comprising $\text{Ca}(\text{OH})_2$ and/or $\text{Mg}(\text{OH})_2$ and a liquid rich in metal and non-metal ions. Upon filtration, the solid comprising $\text{Ca}(\text{OH})_2$ and/or $\text{Mg}(\text{OH})_2$ can be further refined prior to sale. The pH 12 filtrate rich in metal and non-metal ions can be subjected to electrodialysis or an electrolyzer to generate acid (which can be sold) and base solution to be subsequently used in the process.

[00195] In the above two procedures, the acidic drainage is either directly treated through electrolysis (procedure 3) or through adding base (procedure 4).

[00196] In procedure 3, during the electrolysis, either metal or metal hydroxides are being deposited out from the cathode side, whose pH increases over time, while acid is being generated on the anode side, along with oxygen evolution reaction. The acid drainage will end up as a metal-free solution and the pH will be slightly basic, which can be neutralized by the acid generating on the anode side before safe discharge. The acid generated on the anode side can be sold for other industrial purposes.

[00197] In procedure 4, acid and base are generated through electrolysis or electrodialysis of a salt solution like Na_2SO_4 . The acid will be a product for sale. The base is used for neutralizing the mine drainage and precipitate out metal hydroxides. Different metal hydroxide will come out at different pH values. After filtering out all metal hydroxides, the filtrate is an alkaline salt solution. It can be neutralized with the acid from the electrolyzer/electrodialysis and then the neutral salt solution can be salt-split again to regenerate acid and base.

[00198] Throughout the above two processes, the metallic contents are extracted from the mine drainage. The acid from the drainage is separated through the electrolyzer/electrodialysis process, and the base is generated and consumed internally.

Example 3. Model study: removal of select metal ions in an H-type electrolyzer

[00199] Described herein are model studies demonstrating the removal and in some cases

isolation of metals from the catholyte reservoir of an H-type electrolyzer (FIG. 6). Table 1 shows the parameters for each of these studies. In all studies, the anolyte (the solution in the anode reservoir) was 0.1 M Na₂SO₄, and the catholyte (solution within the cathode reservoir) was varied from NiSO₄, a 1:1 mixture of NiSO₄ and CoSO₄, FeSO₄ in H₂SO₄ and a 4:1:1 mixture of FeSO₄:CuSO₄: ZnSO₄ in H₂SO₄.

Table 1. Experimental parameters for model studies in H-type electrolyzer

	Ni only	Ni /Co no cutoff	Ni /Co with cutoff	Fe in acid	Fe/Cu/Zn In acid
Cathode	Titanium foil (2x2 cm ²)				
Anode	DSA mesh				
Catholyte	0.1M NiSO ₄ 50 mL	0.1M NiSO ₄ + 0.1M CoSO ₄ , 50 mL	0.1 M NiSO ₄ + 0.1 M CoSO ₄ , 50 mL	20 mM FeSO ₄ + 80 mM H ₂ SO ₄ , 30 mL	20 mM FeSO ₄ + 5 mM CuSO ₄ + 5 mM ZnSO ₄ + 70 mM H ₂ SO ₄ , 30 mL
Anolyte	0.1M Na ₂ SO ₄				
Membrane	AEM				
Stir rate/T	300 rpm, room temperature				
Applied current	-10 mA	-20mA	-20 mA (2 parts)	-20 mA	-20 mA
Duration/h	25.95	28.95	33.63	6.75	7.54
Cation deletion time	26.67 h			8.04 h	
Termination criteria	full cell voltage overload				

[00200] The performance metrics were:

$$\text{Metal removal EFF (\%)} = ([M^{2+}]_{\text{Initial}} - [M^{2+}]_{\text{Final}}) \times V \times 100\% / [M^{2+}]_{\text{Initial}} \times V \quad (\text{Eq.4})$$

where EFF: efficiency; $[M^{2+}]_{\text{Initial}}$: initial metal ion concentration; $[M^{2+}]_{\text{Final}}$: final metal ion concentration; and V is electrolyte volume.

$$\text{Faradaic efficiency (\%)} = 2 \times F \times ([M^{2+}]_{\text{Initial}} - [M^{2+}]_{\text{Final}}) \times V \times 100\% / Q \quad (\text{Eq.5})$$

where 2: number of electrons transferred in $M^{2+} + 2e^- \rightarrow M$; F: Faradays constant; and Q: total charge passed.

$$\text{Energy consumption (kWh/kg M)} = \int P dt / ([M^{2+}]_{\text{Initial}} - [M^{2+}]_{\text{Final}}) \times V \times MW$$

(Eq. 6)

Where P: power and MW: molar weight of metal ion

Ni only:

[00201] As shown in FIG. 7A, the cathode potential stayed relatively steady around -1.07 V vs. Ag/AgCl throughout the depletion process (± 150 mV). The increase in power consumption over time (FIG. 7B) was consistent with depletion of NiSO₄ in the catholyte solution. The first 15.6 h resulted in 58.2% of Ni²⁺ removal), with the power remaining under 0.0755 W.

[00202] As shown in FIG. 8, the concentration of Ni²⁺ decreased linearly with time, as predicted by Faraday's law. The Ni²⁺ removal efficiency was calculated by Eq. 4 to be $\geq 98\%$. The total Faradaic efficiency (FE) for Ni²⁺ removal was about 100%, with 7.13 kWh/Kg Ni recovered. XRPD analysis of the material deposited on the cathode established it to be 100% crystalline Ni (FIG. 9).

Ni + Co:

[00203] As shown in FIG. 10A, there appeared to be three regions in cathode potential (WE), which were I: -0.73 V vs. Ag/AgCl; II: -0.87 V vs. Ag/AgCl; and III: -1.02 V vs. Ag/AgCl. It was hypothesized that region I and region II corresponded to deposition of Co and Ni, respectively, on the cathode. Accordingly, repeating the experiment with a cathode potential cutoff upon completion of phase I (FIG. 10B), followed by replacement with a fresh cathode, then application of current for the second phase resulted in cathode potentials of: I: -0.70 V vs. Ag/AgCl; and II: -0.82 V vs. Ag/AgCl. FIGs 11A and 11B show the energy consumption without and with cathode potential cutoff, respectively. Without potential cutoff, the first 17.3 h resulted in 56.5% of metal [Ni²⁺ + Co²⁺] being removed, with power less than 0.15 W. With potential cutoff, the first 22.0 h resulted in 66.6% of metal [Ni²⁺ + Co²⁺] being removed, with power less than 0.15 W.

[00204] Examination of each metal ion concentration over time from the catholyte without a potential cutoff (FIG. 12A) indicated that Co²⁺ was removed before Ni²⁺, with the FE for removal of both ions (FIG. 12B) being linear. The removal efficiency was 83.6% for Ni²⁺ and $\geq 97\%$ for Co²⁺; total FE for [Co²⁺ + Ni²⁺] was 92.5%. Cathode deposits were 69.2 $\pm$ 4.1 wt% Co and 30.8 $\pm$ 3.1 wt% Ni, with 8.07 kWh/Kg [Co²⁺ + Ni²⁺] recovered. FIG. 13A and 13B show

the combined metal depositions on the cathode.

[00205] Examination of each metal ion concentration over time from the catholyte with a potential cutoff (FIG. 14A) indicated that Co^{2+} was removed before Ni^{2+} , with the FE for removal of both ions (FIG. 14B) being linear. Cathode deposition after the potential cutoff was 56.1 ± 6.3 wt% Co and 43.9 ± 6.0 wt% Ni. FIG. 15 shows the total metal deposition on the cathode prior to the potential cutoff, and FIG. 16 shows the cathode surface after potential cutoff. Removal efficiency after cutoff were 90.8 % Ni^{2+} and ≥ 97 %; total FE for $[\text{Co}^{2+} + \text{Ni}^{2+}]$ was 80.7%. Cathode deposition after potential cutoff was 56.1 ± 6.3 wt% Co and 43.9 ± 6.0 wt% Ni, with 8.98 kWh/Kg $[\text{Co}^{2+} + \text{Ni}^{2+}]$ recovered.

Fe in acid:

[00206] As shown in FIG. 17A, the cathode potential stayed relatively steady around -0.88 V vs. Ag/AgCl (± 20 mV) in the first 3.56 h. The energy consumption (FIG. 17B) remained less than about 15 W for the first 3.9 h but increased, which was consistent with Fe levels in the catholyte becoming depleted. Depletion of Fe^{2+} from the catholyte was confirmed qualitatively by UV-vis (FIG. 18A), with no crossover of Fe^{2+} observed in the anolyte. There was 83.8% reduction in acidity in the catholyte (FIG. 18B). Elemental iron was deposited on the cathode after the run was completed (FIG. 19A), which formed an oxide coating after 18 h of contact with air (FIG. 19B). Characterization of the cathode with deposited Fe by scanning electron microscope/energy-dispersive X-ray spectroscopy (SEM-EDS) and elemental composition of metallic content, respectively, are shown in FIGs. 20A and 20B.

Fe plus Cu plus Zn in acid:

[00207] As shown in FIG. 21A, the cathode potential showed two regions: I: -0.63 to about -0.80 V vs. Ag/AgCl and II: -1.50 to about -1.83 V vs. Ag/AgCl. The energy consumption (FIG. 21B) showed the first 4.8 h to be less than 0.15W, with an increase after that consistent with depletion of metal ions. Significant removal of $\text{Fe}^{2+} + \text{Cu}^{2+}$ from the catholyte was confirmed qualitatively by UV-vis (FIG. 22A), with no crossover of Fe^{2+} or Cu^{2+} observed in the anolyte. There was 88.0% reduction in acidity in the catholyte (FIG. 22B).

[00208] The examples disclosed herein provide support for the utility of the methods described herein for removal of metallic ion content from aqueous media.

[00209] Particular embodiments of the subject matter have been described. Other

embodiments are within the scope of the following claims. For example, the actions recited in the claims can be performed in a different order and still achieve desirable results. As one example, the processes depicted in the accompanying figures do not necessarily require the particular order shown, or sequential order, to achieve desirable results. In some cases, multitasking and parallel processing may be advantageous.

WHAT IS CLAIMED IS:

1. A method of reducing chemical content in acidic mine waste comprising one or more target ions, the method comprising:

(a) contacting the acidic mine waste with a base to form modified acidic waste and optionally insoluble salts of one or more target ions;

(b) contacting the modified acidic waste with an electrolyzer to form (i) a base or a product comprising insoluble salts of one or more target ions, or metallic deposition on the cathode of one or more target ions, and (ii) an acid.

(c) optionally repeating step (a) at least once, wherein the base of repeated step (a) comprises the base of step (b)(i).

2. A method of reducing chemical content in acidic mine waste comprising one or more target ions, the method comprising:

(a) contacting the acidic mine waste with a base and carbon dioxide to form (i) insoluble carbonate salts of one or more target ions; and (ii) a solution rich in ions;

(b) contacting the solution rich in ions of step (a)(ii) with an electrolyzer to regenerate (i) a base and (ii) an acid; and

(c) optionally repeating steps (a) and (b), wherein the base of repeated step (a) comprises the regenerated base of step (b)(i).

3. The method of claim 1 or 2, wherein step (c) is repeated at least once.

4. The method of claim 1 or 2, wherein step (c) is performed continuously.

5. The method of claim 1 or 2, wherein step (a) comprises sequentially contacting the acidic waste comprising the one or more ions with two or more independently selected bases.

6. The method of claim 1, further comprising separating the insoluble salts of metallic deposition of step (b)(i) from the acid of step (b)(ii) prior to step (c).

7. The method of claim 2, further comprising separating the insoluble salts or metallic deposition from the acid of step (b)(ii) prior to step (c).

8. A method of reducing chemical content in acidic mine waste comprising one or more target ions, the method comprising:

- (a) contacting the acidic mine waste with an electrolyzer to form (i) an acid and (i) metal hydroxides or metallic deposition on the cathode of one or more target ions; and
- (b) collecting the metal hydroxide or the metallic deposition of step (a).

9. A method of reducing chemical content in acidic mine waste, the method comprising:

contacting the acidic mine waste comprising one or more target ions with a base in an electrochemical cell to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, and the electrochemical cell regenerates the base and forms an acidic product comprising the one or more ions and optionally insoluble salts thereof;

wherein the electrochemical cell comprises an anode reservoir comprising an anode and the acid, and a cathode reservoir comprising a cathode and the base, wherein the anode reservoir and the cathode reservoir are separated by a separator.

10. A method of reducing the environmental impact of acidic mine waste, the method comprising:

(a) contacting the acidic mine waste comprising one or more target ions with a base to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof;

(b) contacting the modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, with an electrolyzer to regenerate the base and form an acidic product comprising the one or more ions and optionally insoluble salts thereof, and

(c) repeating step (a) at least once, wherein the base of repeated step (a) comprises the base of step (b).

11. The method of any one of claims 1-10, further comprising setting a potential cutoff to the electrolysis to target a specific metallic deposition of one or more metals on the cathode.

12. The method of any one of claims 1-11, wherein the electrolyzer is a single-membrane electrolyzer, two-membrane salt splitting electrolyzer, a multi-membrane salt-

splitting electrolyzer, a chlor-alkali electrolyzer, a bipolar membrane electrodialysis electrolyzer, or a combination of any of the foregoing.

13. The method of any one of claims 1-12, wherein the base comprises a carbonate salt and/or a bicarbonate salt.

14. The method of claim 13, wherein the carbonate salt and/or the bicarbonate salt is selected from sodium, potassium, lithium, and combinations of any of the foregoing.

15. The method of any one of claims 2-14, wherein the carbon dioxide is provided as a composition, wherein the composition comprises carbon dioxide and at least one additional gas.

16. The method of claim 15, wherein the composition comprises carbon dioxide in an amount of about 0.01 wt% to about 99.9 wt%, or about 0.01 wt% to about 1.5 wt%, or about 1 wt% to about 10 wt%, or about 50 wt% to about 90 wt%.

17. The method of any one of claims 1-16, further comprising repeating each of the electrolyzing steps using sequential electrolysis.

18. The method of claim 17, wherein the sequential electrolysis occurs via continuous multi-ion sequential electrowinning.

19. The method of any one of claims 9-18, wherein the separator is an anion exchange membrane.

20. The method of any one of claims 9-18, wherein the separator is a cation exchange membrane.

21. The method of claim any one of claims 9-20, further comprising separating the acidic product from the electrochemical cell.

22. The method of claim any one of claims 9-21, further comprising repeating the contacting at least once using sequential electrolysis.

23. The method of claim 22, wherein the sequential electrolysis occurs via continuous multi-ion sequential electrowinning.

24. The method of any one of claims 1-23, wherein the base is selected from the group consisting of NaOH, LiOH, KOH, Na₂CO₃, and NaHCO₃, or any combination thereof.

25. The method of any one of claims 1-24, wherein the base is NaOH.

26. The method of any one of claims 1-25, wherein the acid is selected from the group consisting of HCl, HNO₃, H₂SO₄, and H₃PO₄, or any combination thereof.

27. The method of any one of claims 1-26, wherein the acid is the acid is HCl or HNO₃, or any combination thereof.

28. A system for reducing chemical content in acidic mine waste, comprising:
an electrochemical cell configured to reduce chemical content in acidic mine waste, wherein the electrochemical cell comprises an anode reservoir comprising an anode and an acid, and a cathode reservoir comprising a cathode and a base, wherein the anode reservoir and the cathode reservoir are separated by a separator;

a contactor configured to input the acidic waste comprising one or more target ions into the cathode reservoir, wherein the cathode reservoir is configured to contact the acidic waste with the base to form modified acidic waste comprising the one or more ions and optionally insoluble salts thereof, and the anode reservoir is configured to contact the modified acidic waste comprising the one or more ions with the acid to form an acidic product comprising the one or more ions and optionally insoluble salts thereof;

a first filtration system in contact with the cathode reservoir configured to filter out any insoluble salts from the modified acidic waste from the cathode reservoir; and

a second filtration system in contact with the anode reservoir configured to filter out any insoluble salts from the acidic product comprising the one or more ions and optionally insoluble salts thereof, from the anode reservoir.

29. The system of claim 28, further comprising a tube connecting from the anode reservoir to the cathode reservoir configured to output hydrogen gas from the cathode reservoir and input hydrogen gas into the anode reservoir.

30. The system of claim 28 or 29, further comprising a conducting material connecting the anode to the cathode configured to output electrons from the anode and input the

electrons to the cathode.

31. The system of any one of claims 28-30, further comprising a valve configured to input water into the anode reservoir.

32. The system of any one of claims 28-31, wherein the separator is an anion exchange membrane or a cation exchange membrane.

33. The method of any one of claims 1-27 or the system of any one of claims 28-32, wherein the one or more ions target ions are metallic ions selected from ions of strontium, barium, radium, aluminum, gallium, indium, tin, thallium, lead, bismuth, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, and mercury.

34. The method or system of any one of claims 1-33, wherein the one or more ions target ions are metallic ions selected from ions of tin, lead, iron, cobalt, nickel, copper, zinc, palladium, and cadmium.

35. The method or system of any one of claims 1-34, wherein the one or more ions are metallic ions selected from ions of cobalt and nickel.

36. The method or system of any one of claims 1-35, wherein the acidic mine waste comprises mine drainage and/or mine tailings.

37. The method or system of any one of claims 1-36, wherein the acidic mine waste is mine drainage and/or mine tailings.

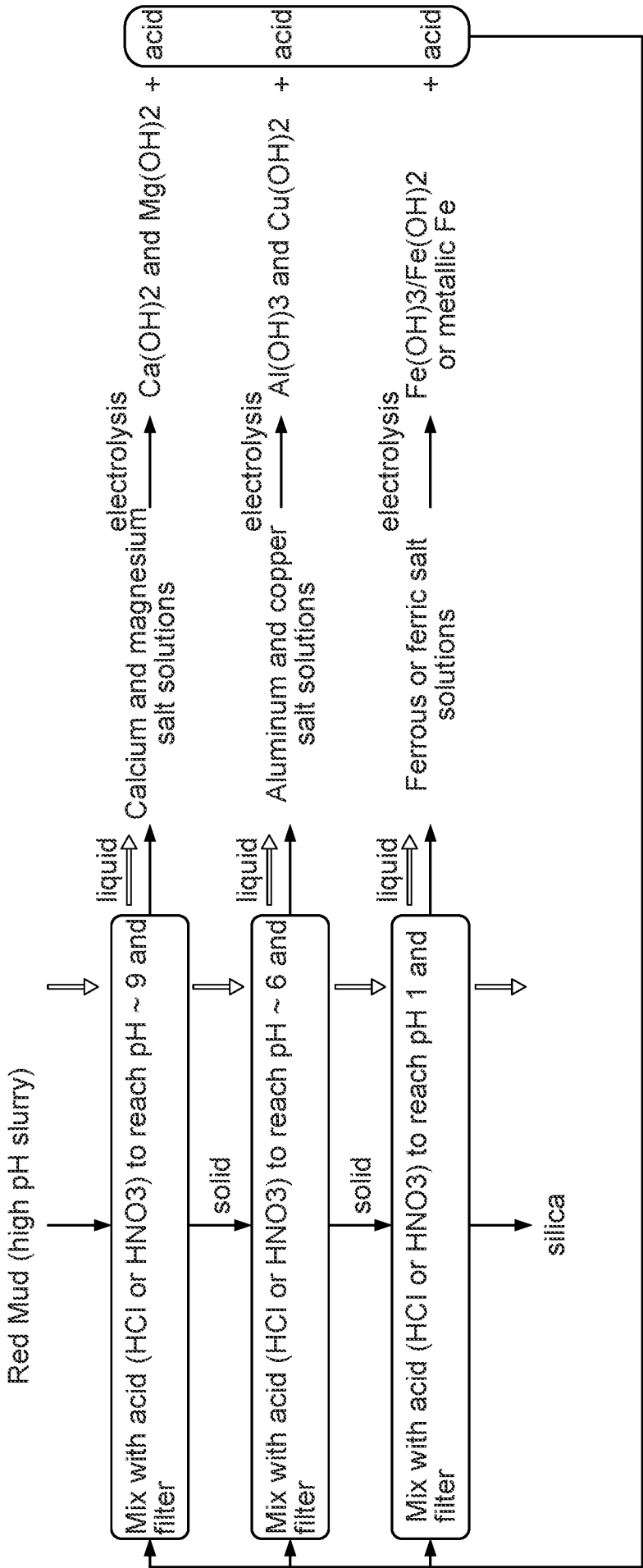


FIG. 1

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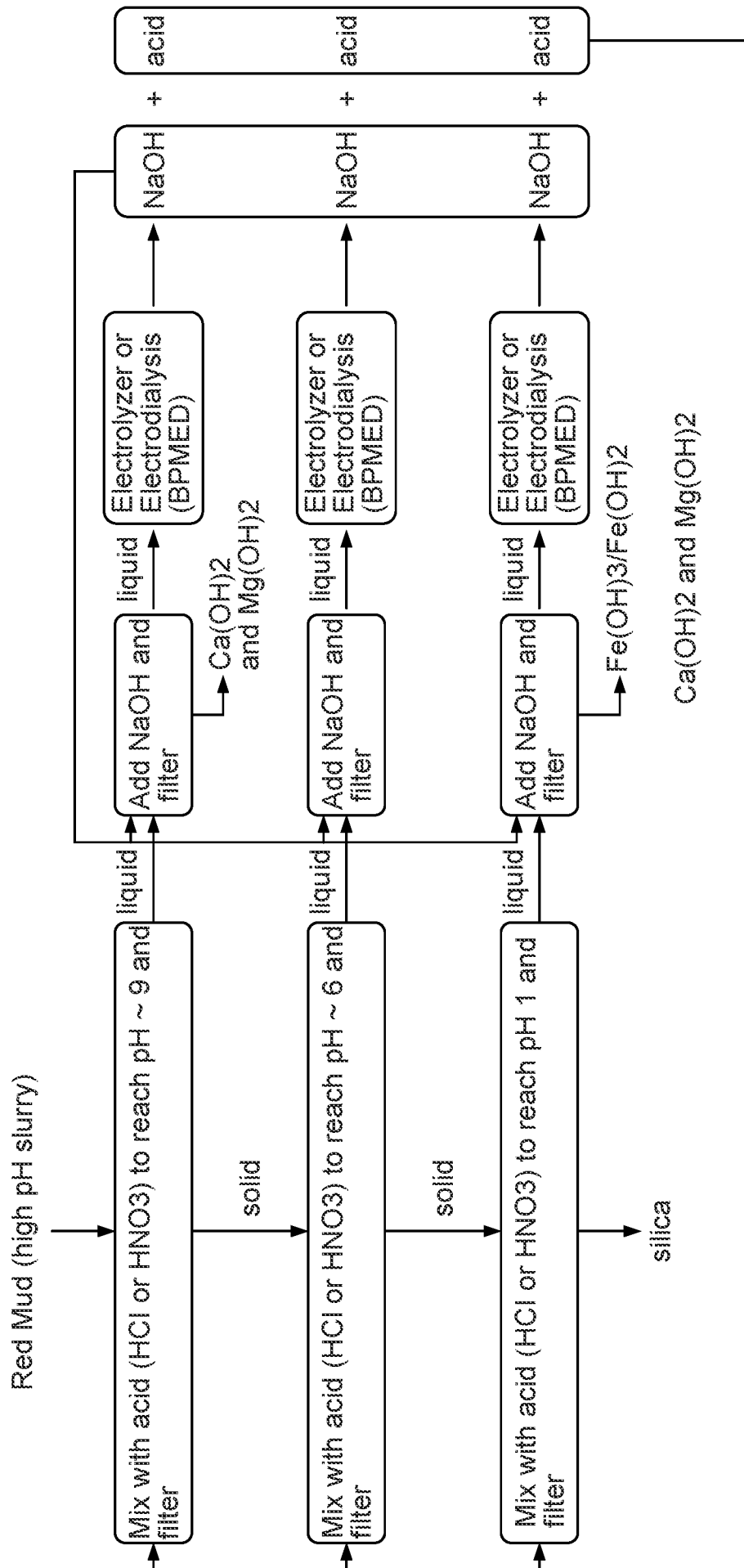


FIG. 2

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Parameter	Mean	Median	No.	S.D.	Min	Max
(I) Raw acid mine drainage						
pH	2.67	2.65	58	0.28	2.1	3.3
Al mg/l	774	517	42	732	57	2211
As µg/l	223	66	41	403	0	1641
Cd µg/l	916	840	58	727	30	2480
Cu mg/l	185	147	58	172	4.5	590
Fe mg/l	996	1029	58	780	24	2384
Zn mg/l	229	208	58	191	16	1074
SO ₄ mg/l	10203	8720	34	6999	1280	24668
Cond. µS/cm	6874	6580	57	3859	1750	15700
AMD _I	9.6	5.4	34	9.0	0.79	28.4

FIG. 3

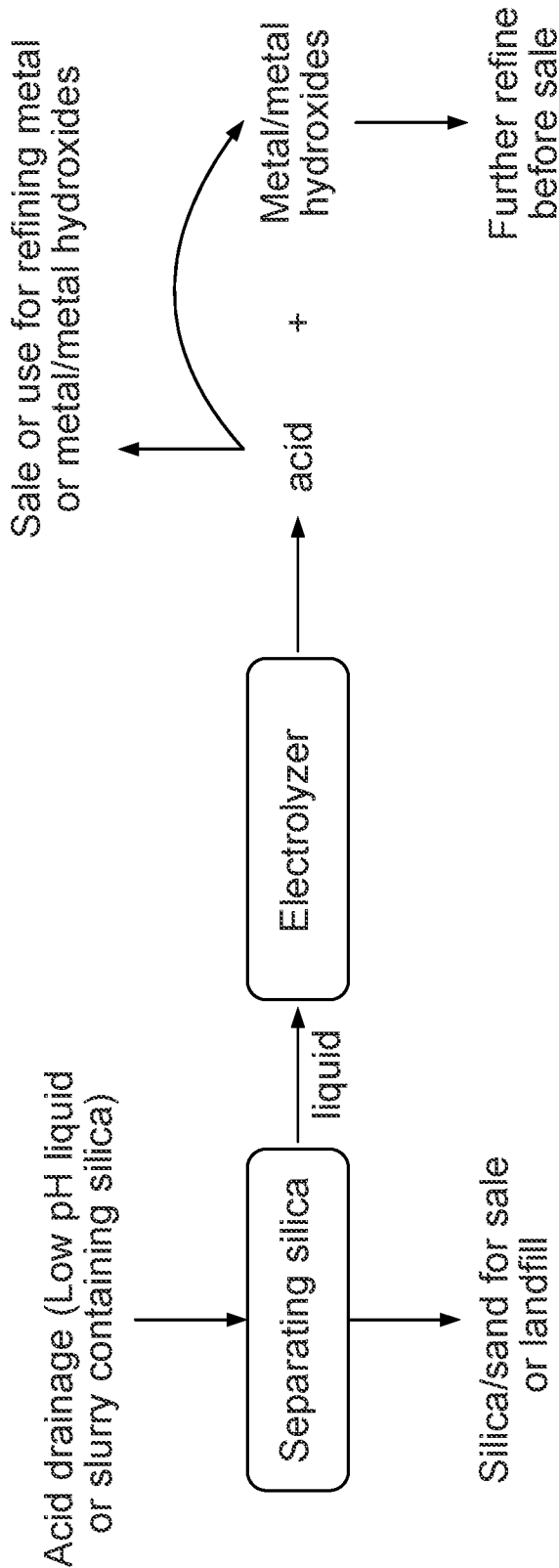


FIG. 4

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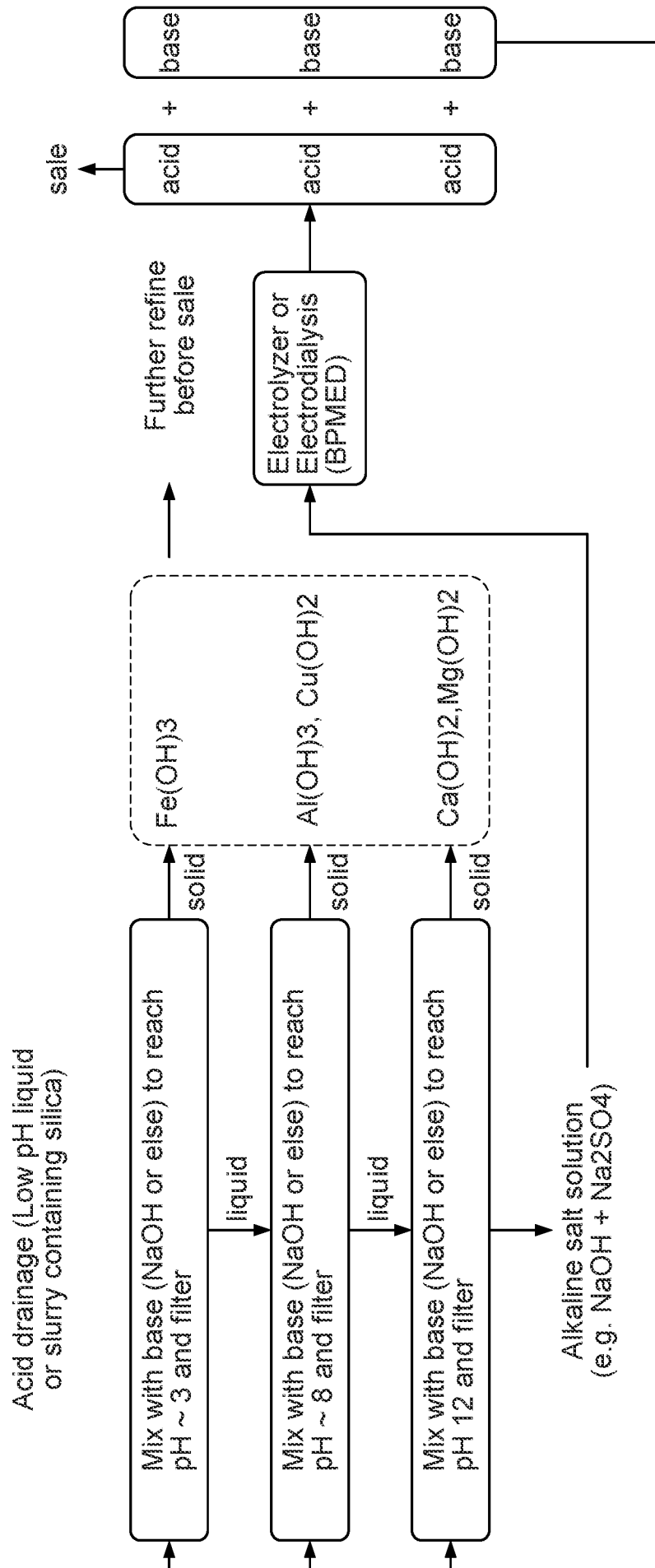


FIG. 5

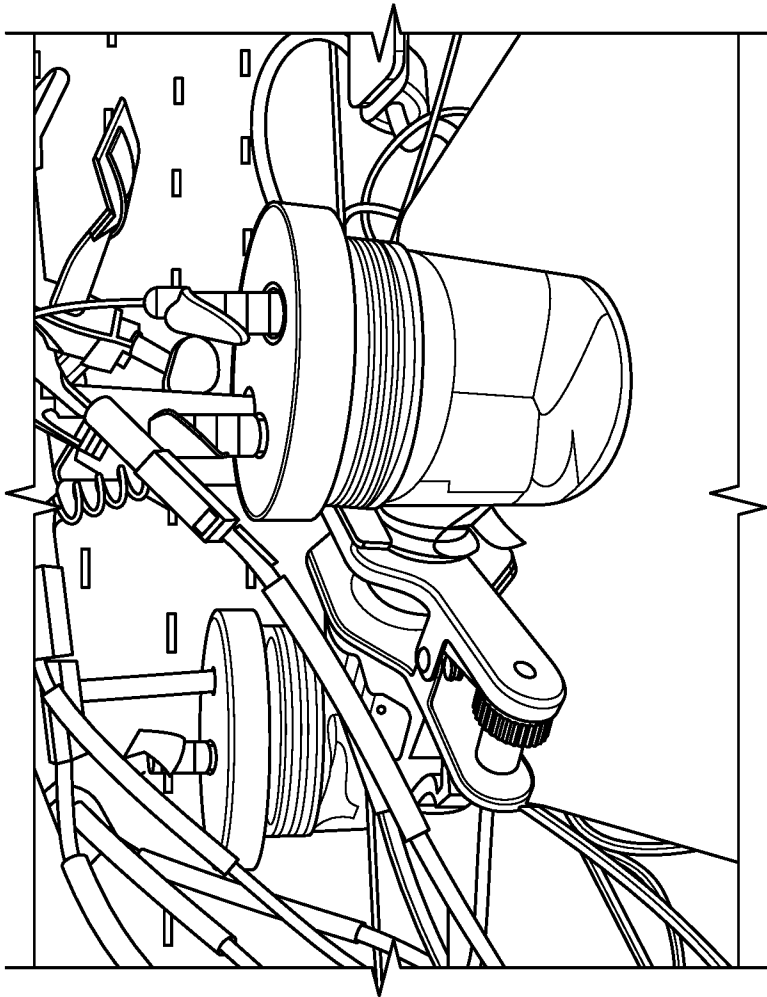
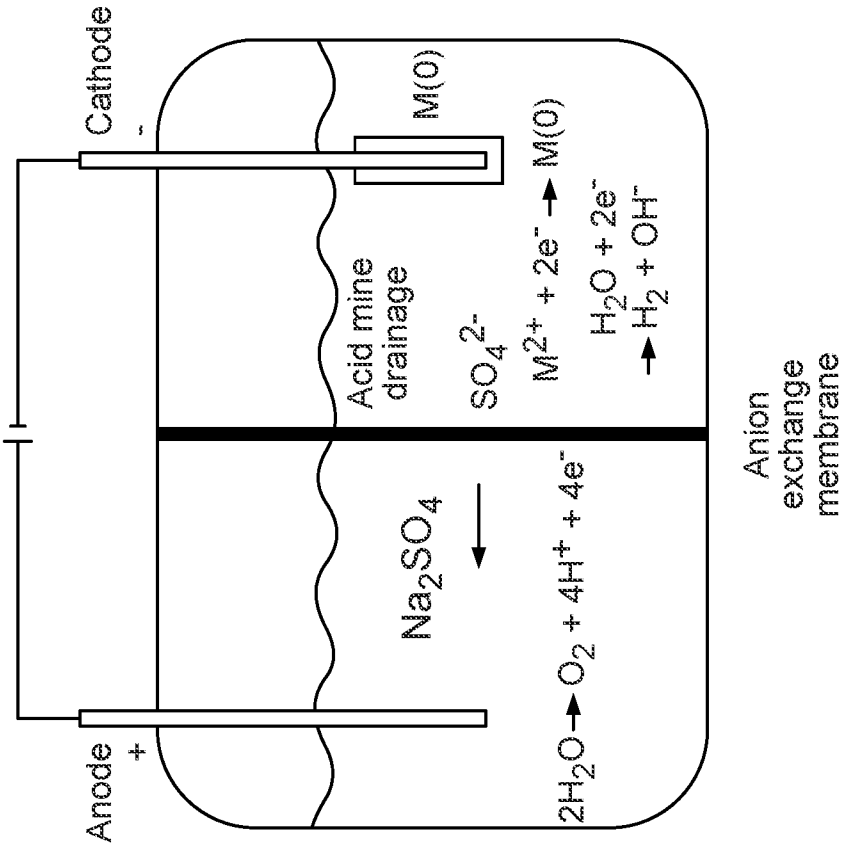


FIG. 6B



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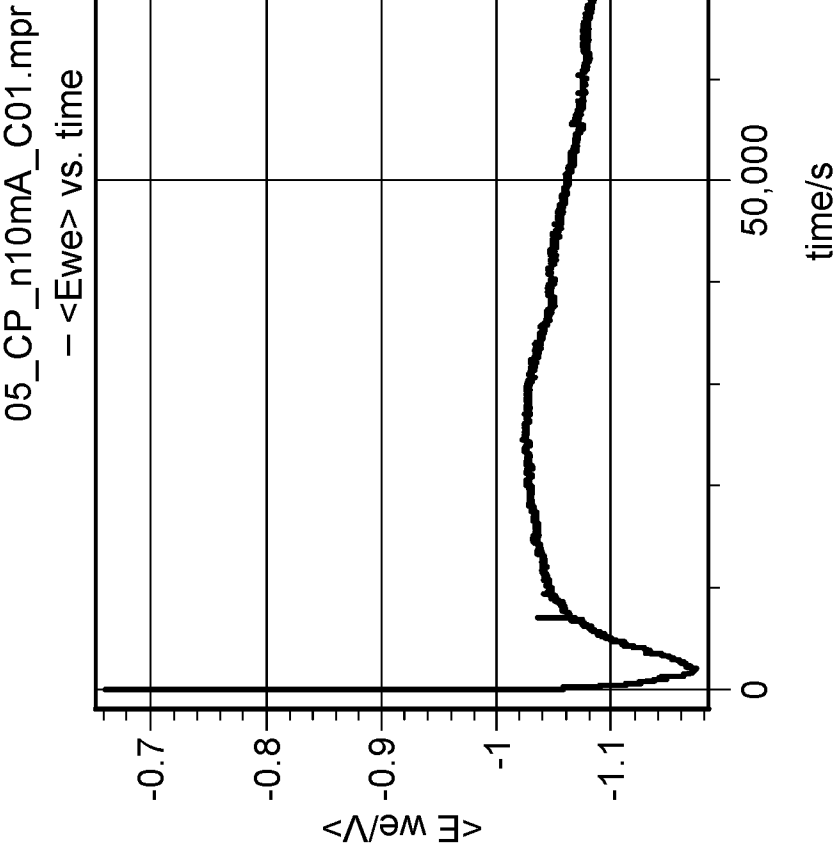


FIG. 7A

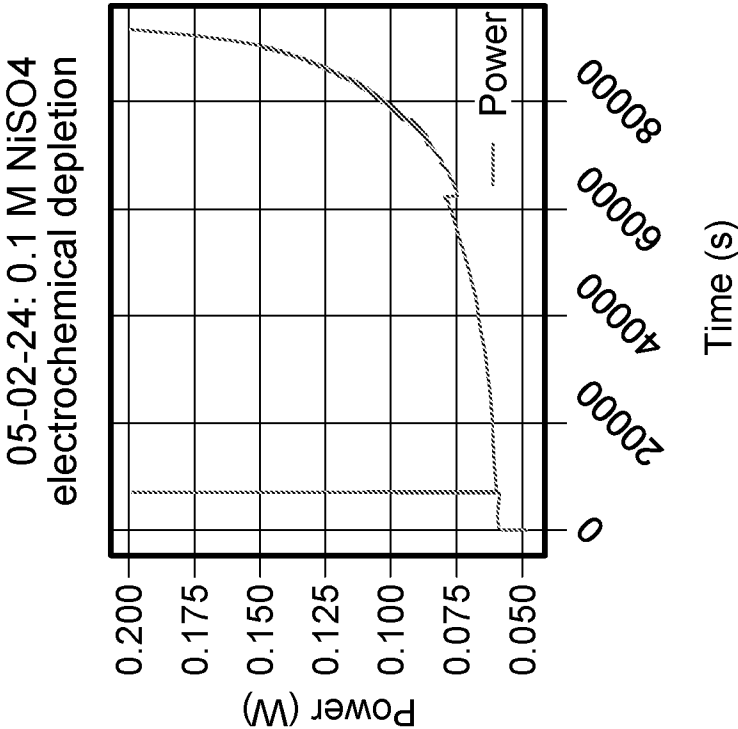


FIG. 7B

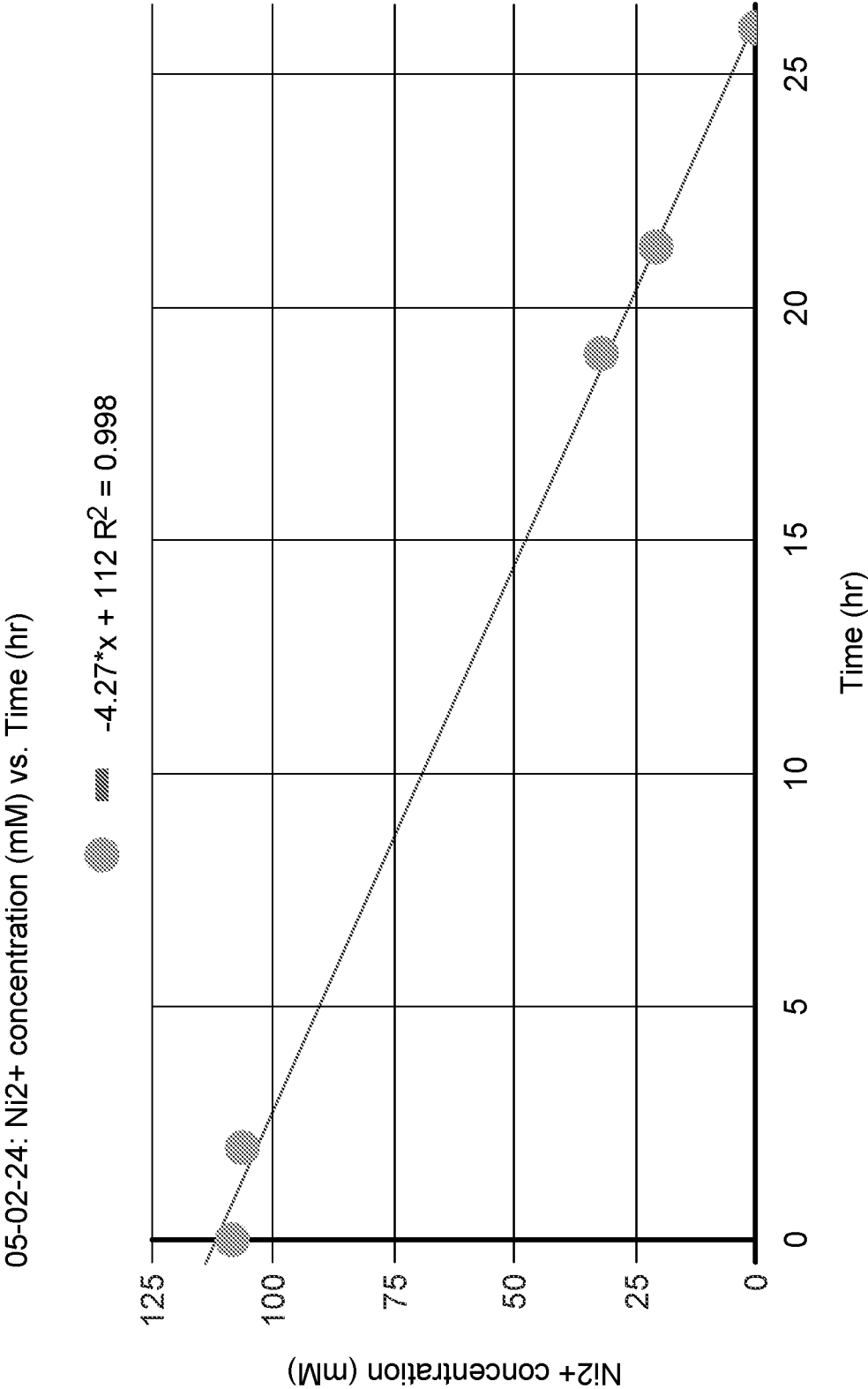


FIG. 8

PDF 04-001-3331 Ni Nickle, syn

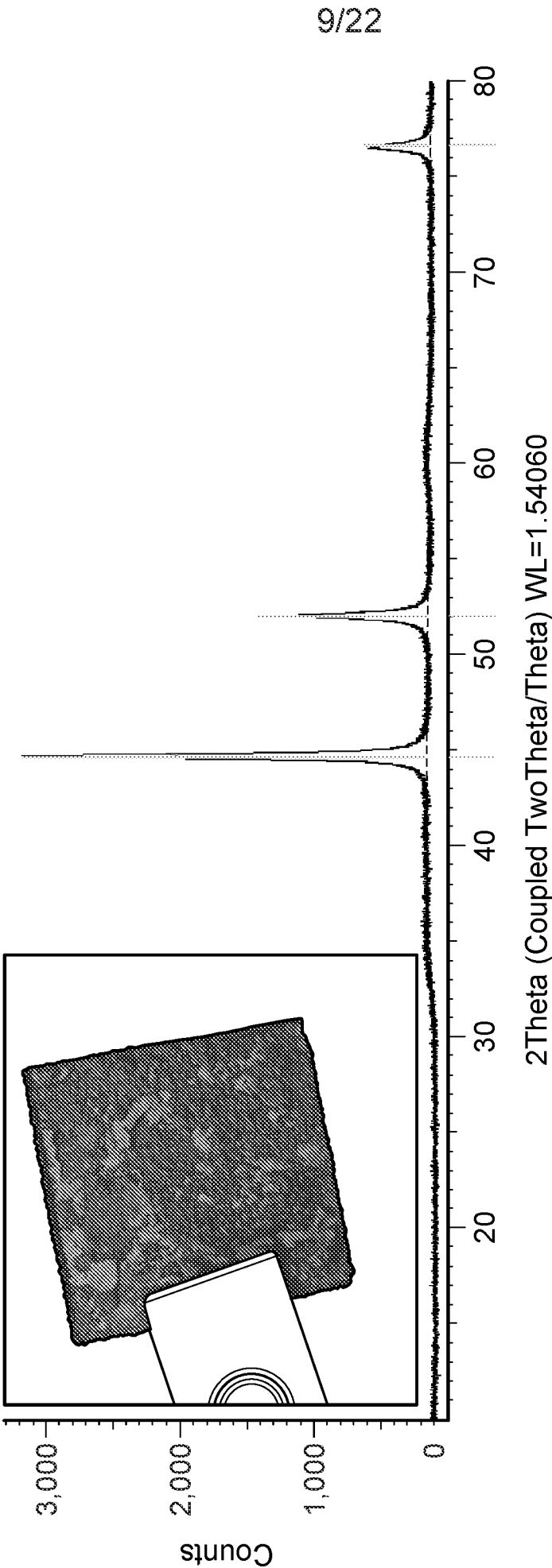


FIG. 9

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05-21-24: 0.1 M NiSO4 + 0.1M CoSO4
electrochemical depletion

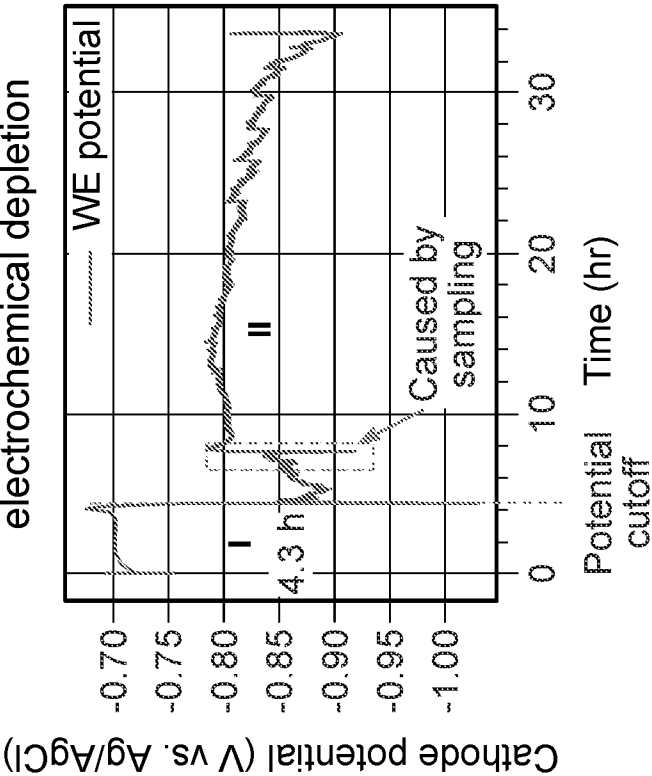


FIG. 10B

08_CP_n20mA_C01.mpr
- <Ewe> vs. time

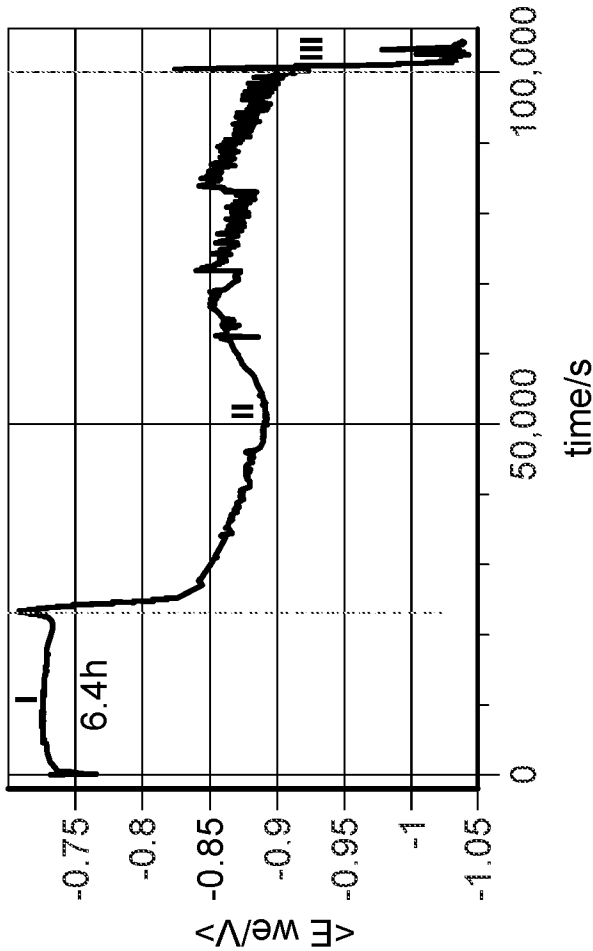


FIG. 10A

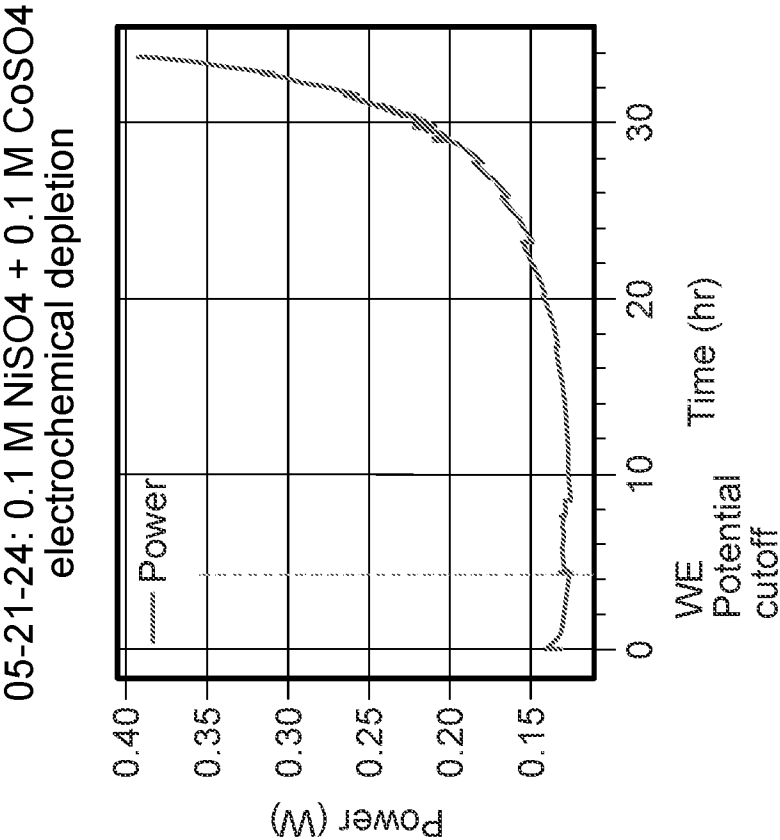


FIG. 11B

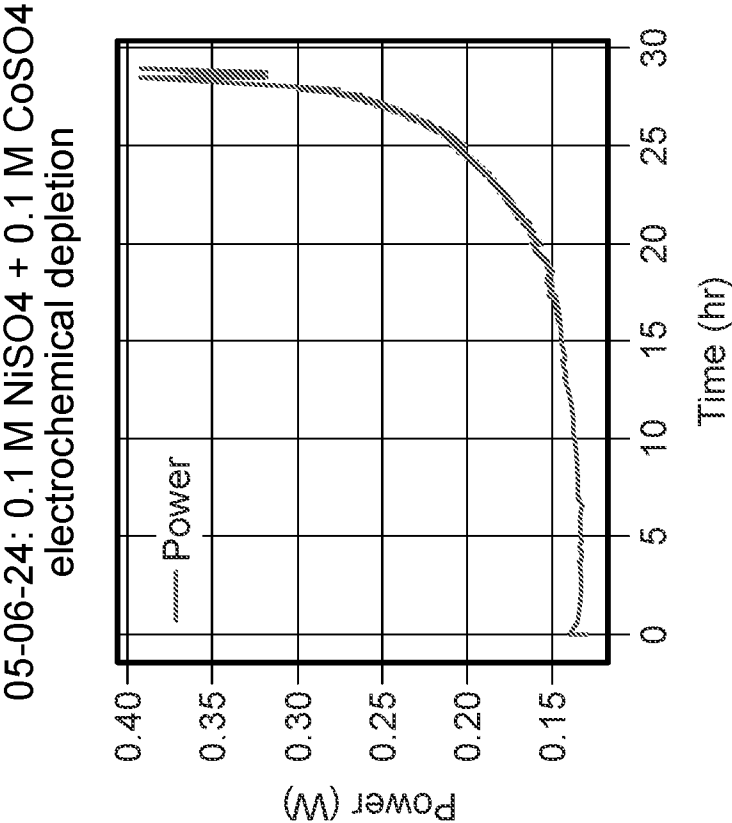


FIG. 11A

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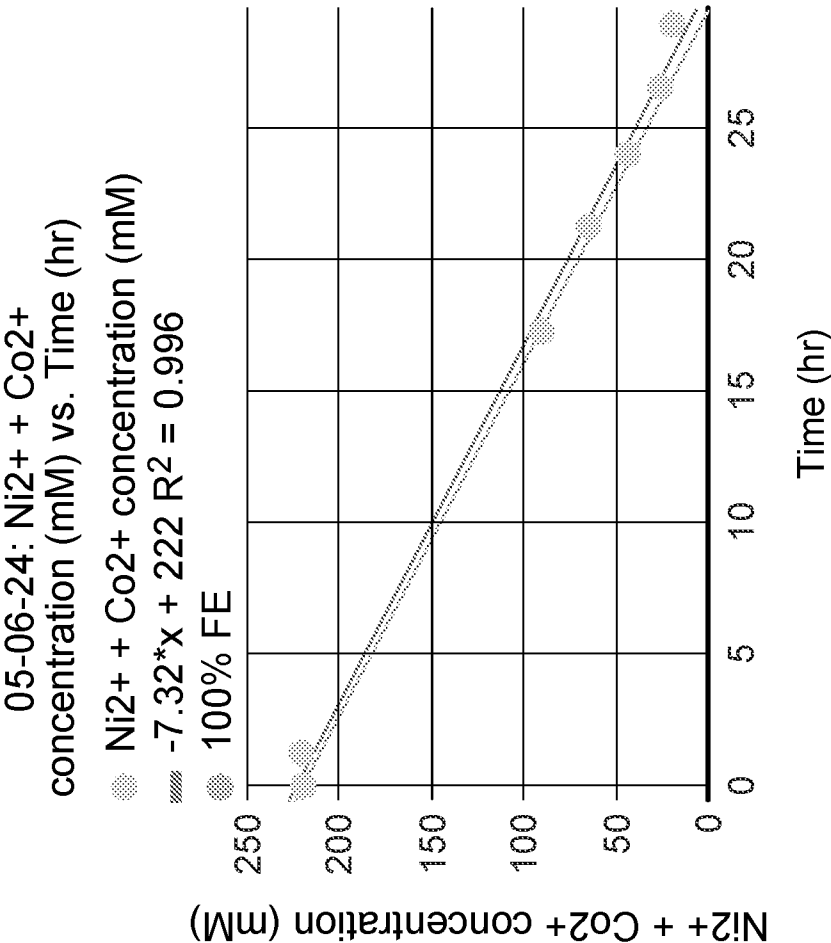


FIG. 12B

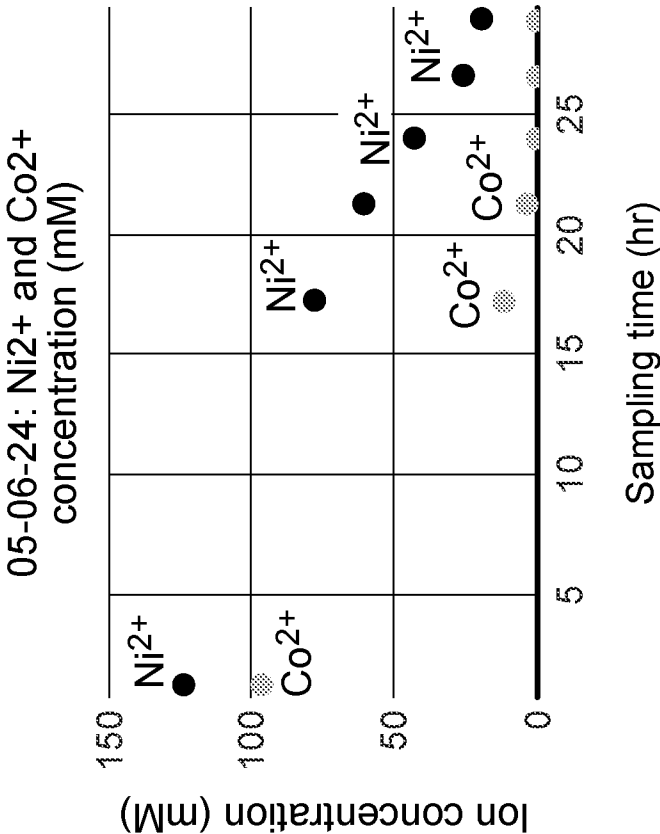


FIG. 12A

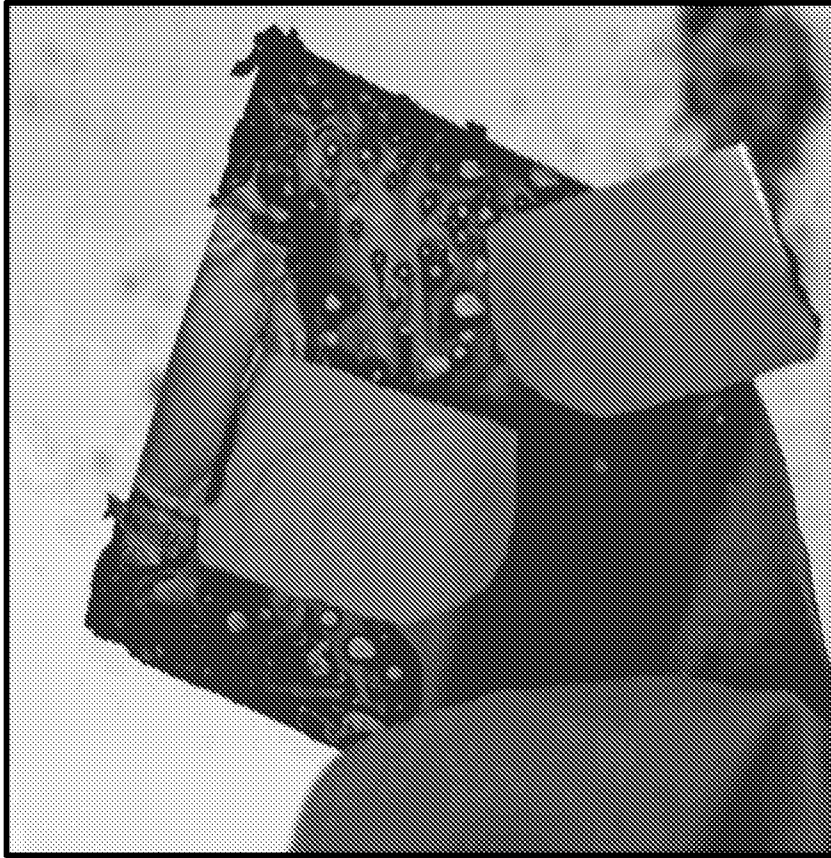


FIG. 13B

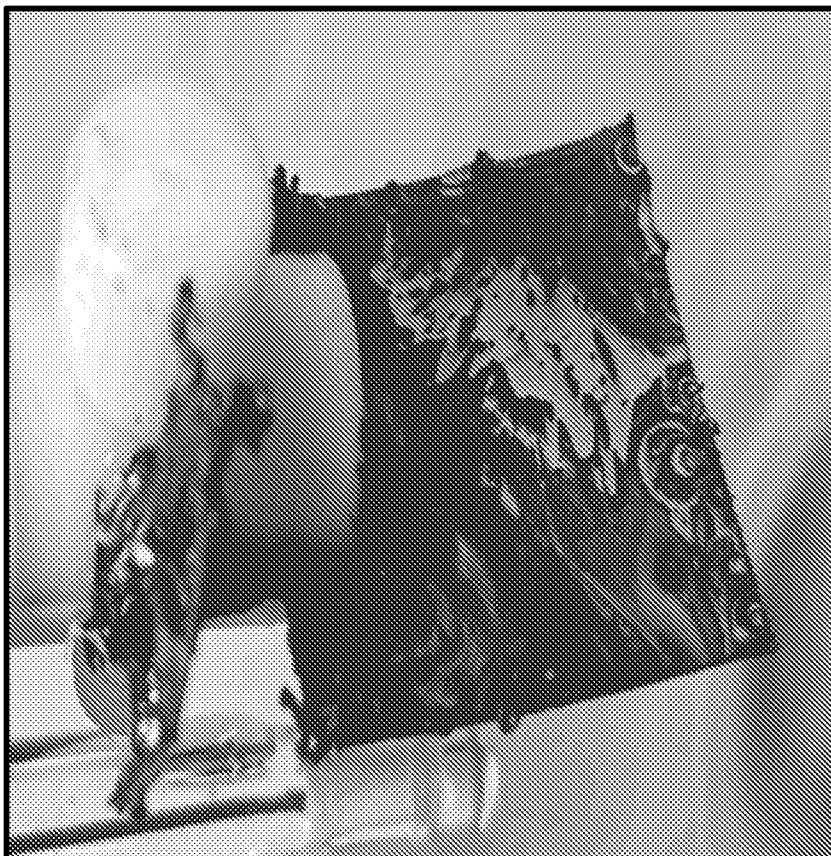


FIG. 13A

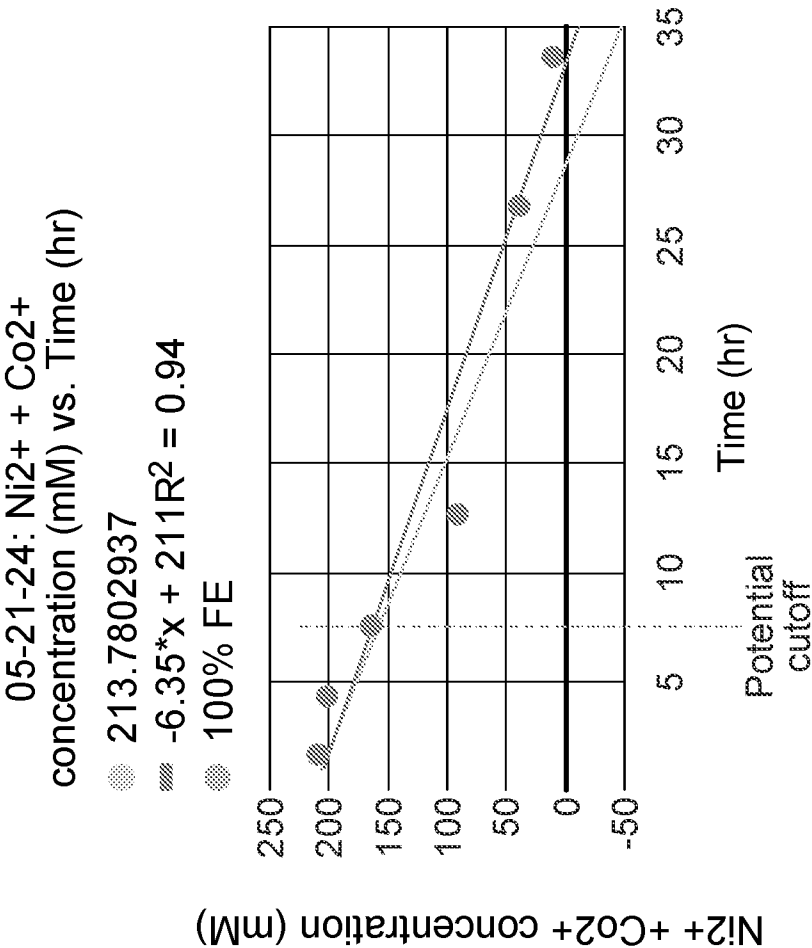


FIG. 14B

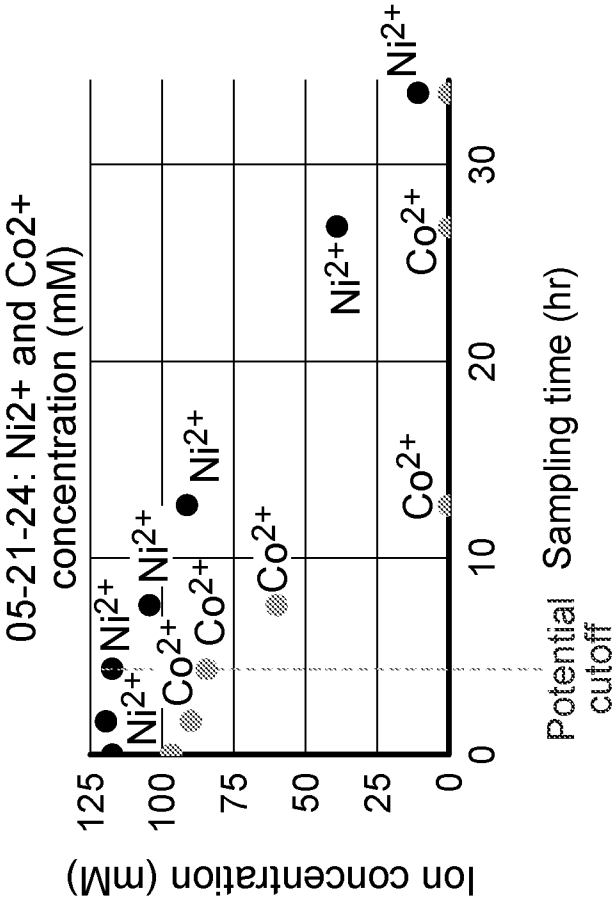


FIG. 14A

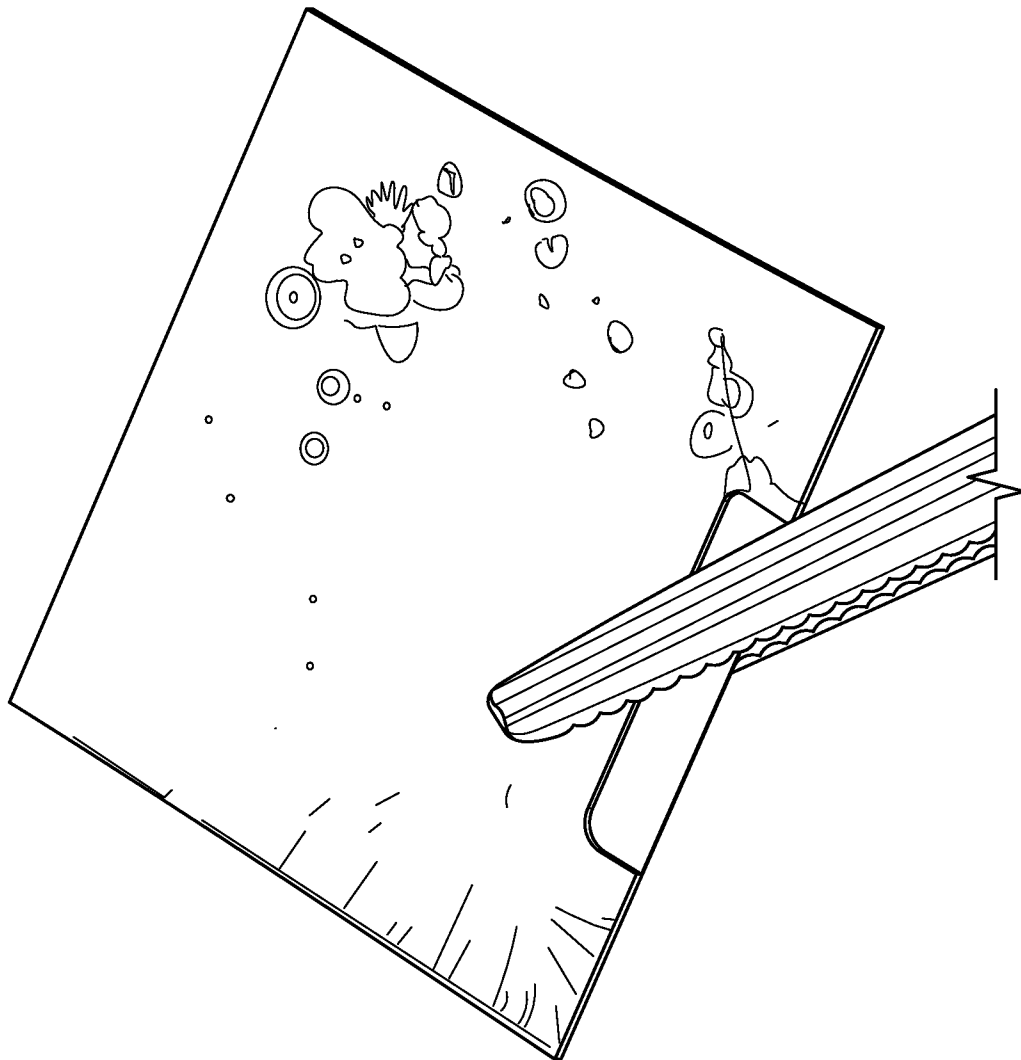


FIG. 15

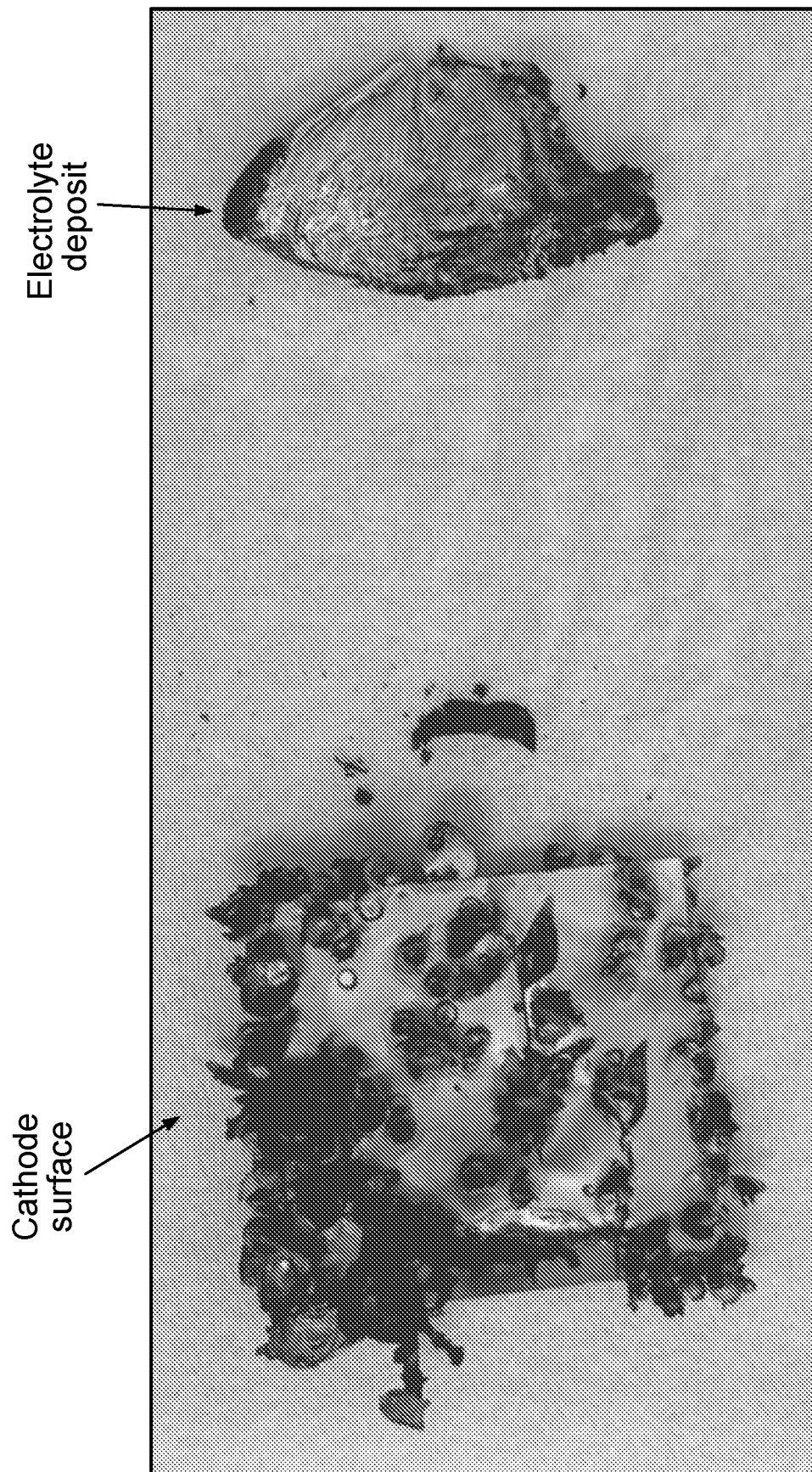


FIG. 16

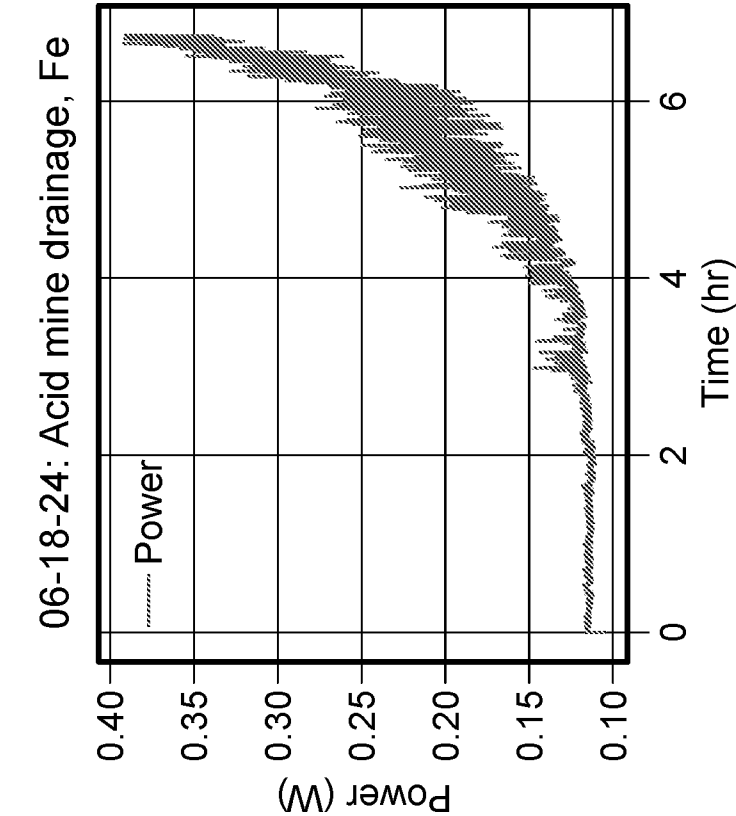


FIG. 17B

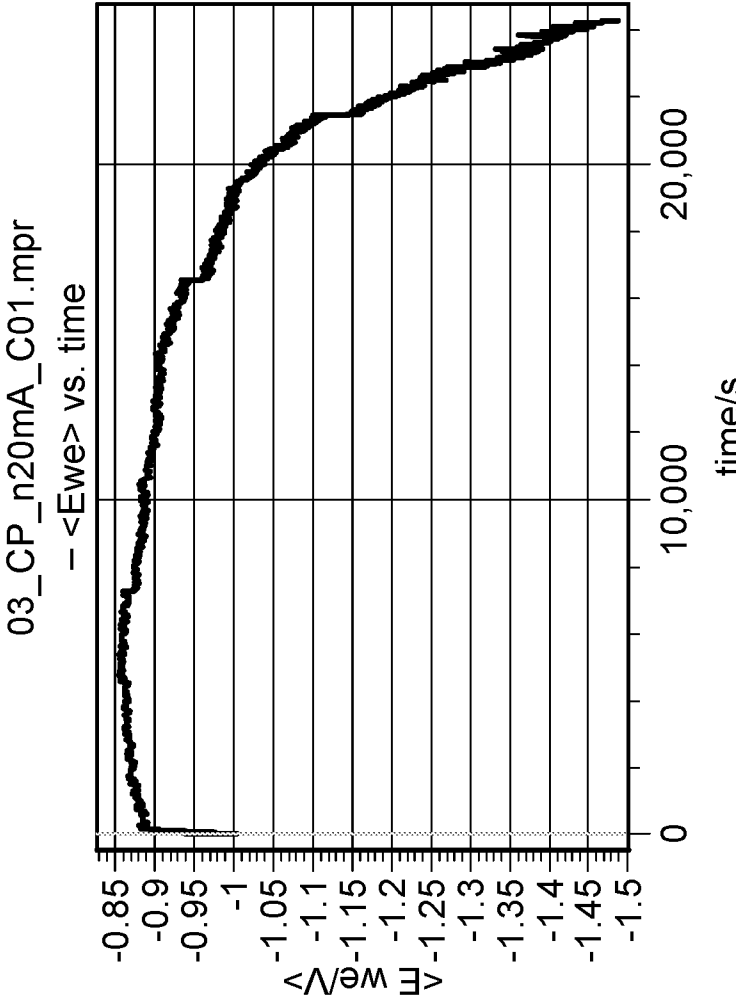


FIG. 17A

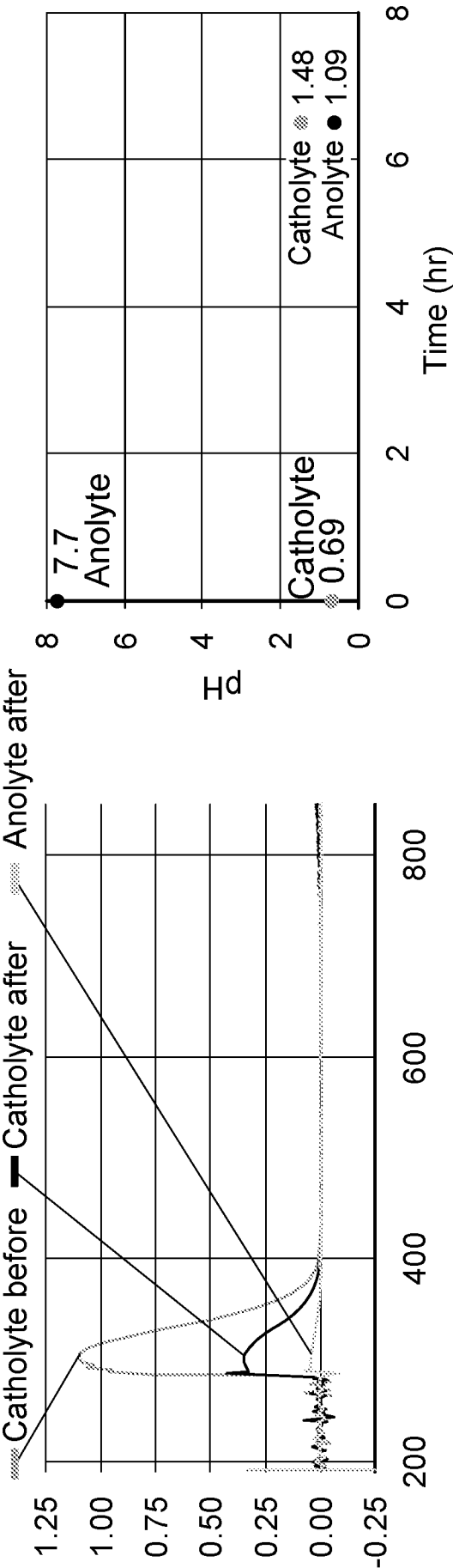


FIG. 18B

FIG. 18A

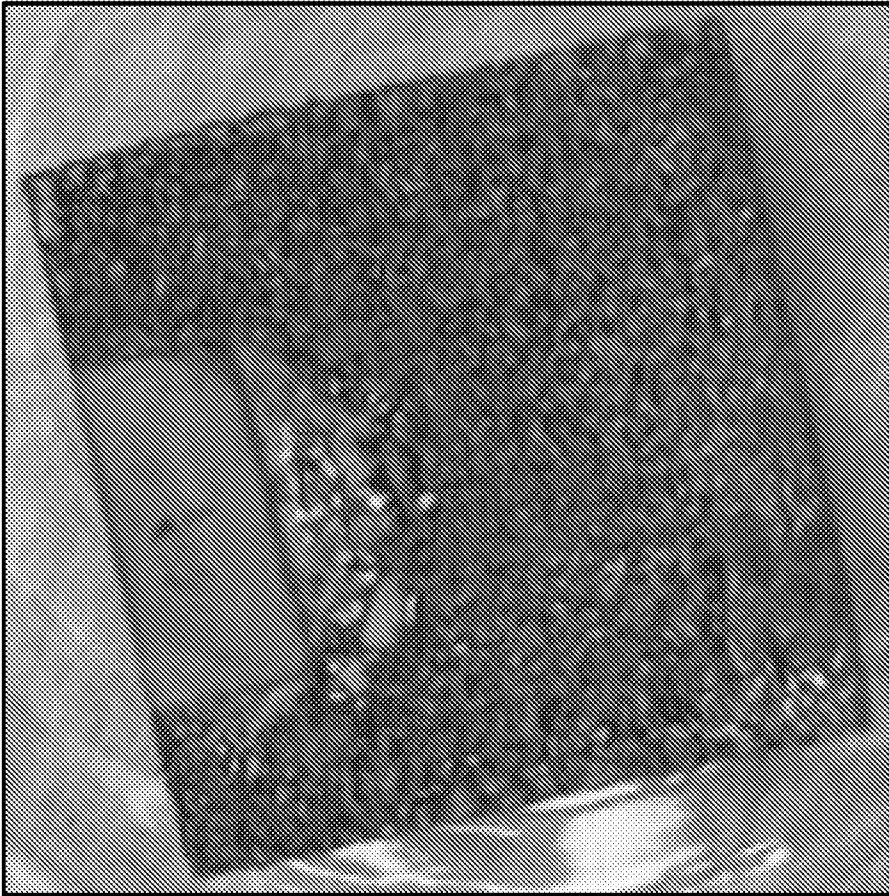


FIG. 19B

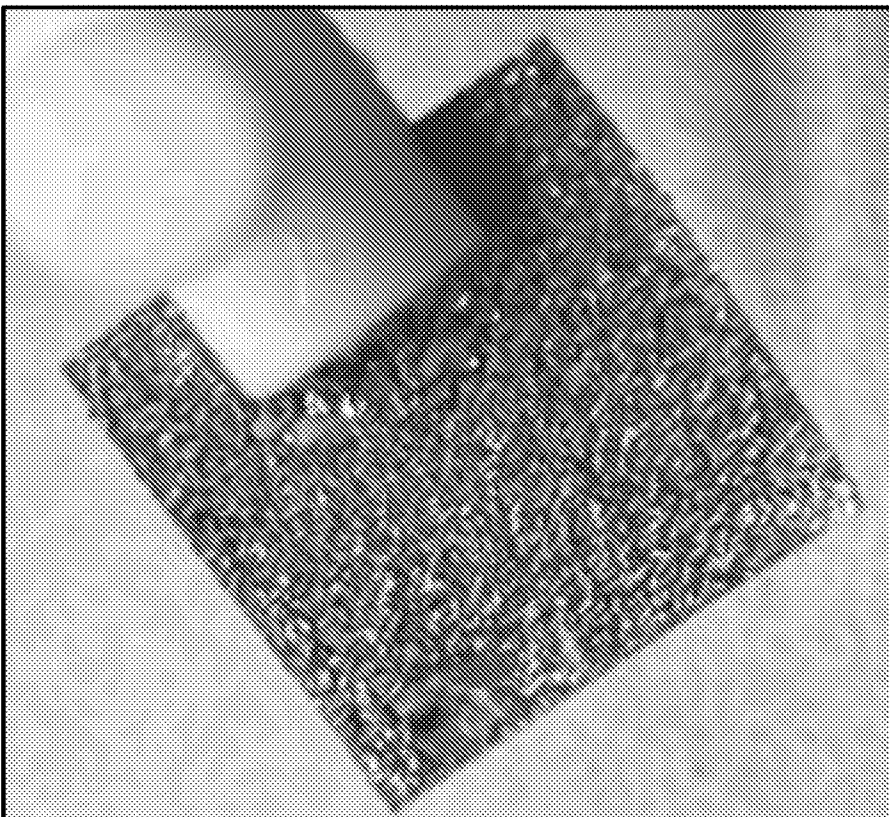


FIG. 19A

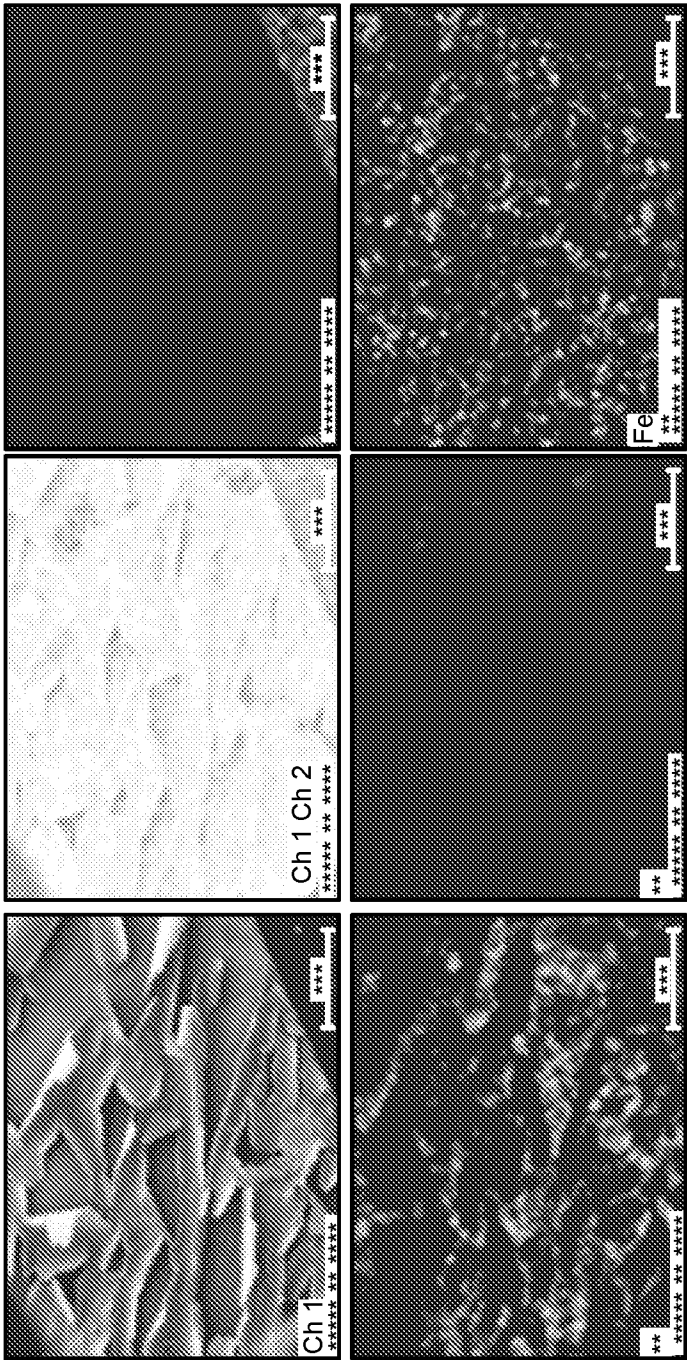


FIG. 20A

Spectrum 1

Element	At. No	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Ti	22	2373	8.54	7.93	6.95	0.49	5.73
Fe	26	6279	85.24	79.12	59.43	6.04	7.09
O	8	8621	13.68	12.69	33.28	0.52	3.80
S	16	164	0.28	0.26	0.34	0.06	20.58
		Sum	107.74	100.00	100.00		

FIG. 20B

05_CP_n20mA_C03.mpr
- <Ewe> vs. time

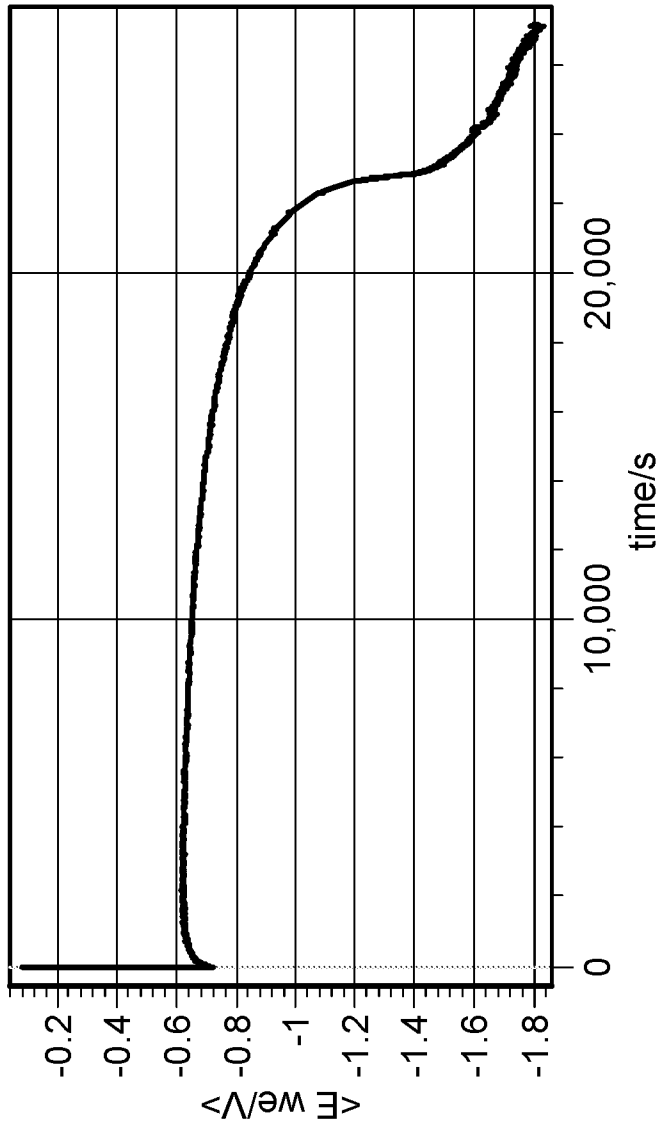


FIG. 21A

06-18-24: Acid mine drainage,
Fe+Cu+Zn

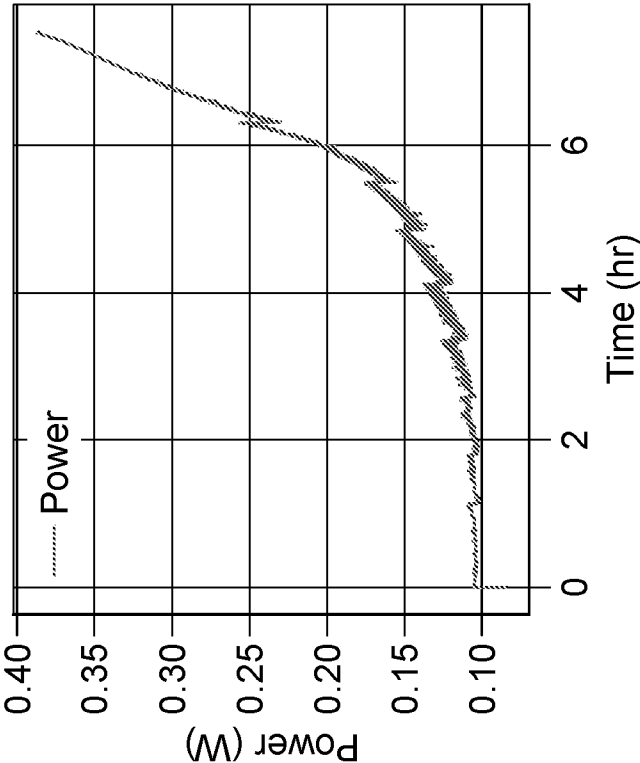


FIG. 21B

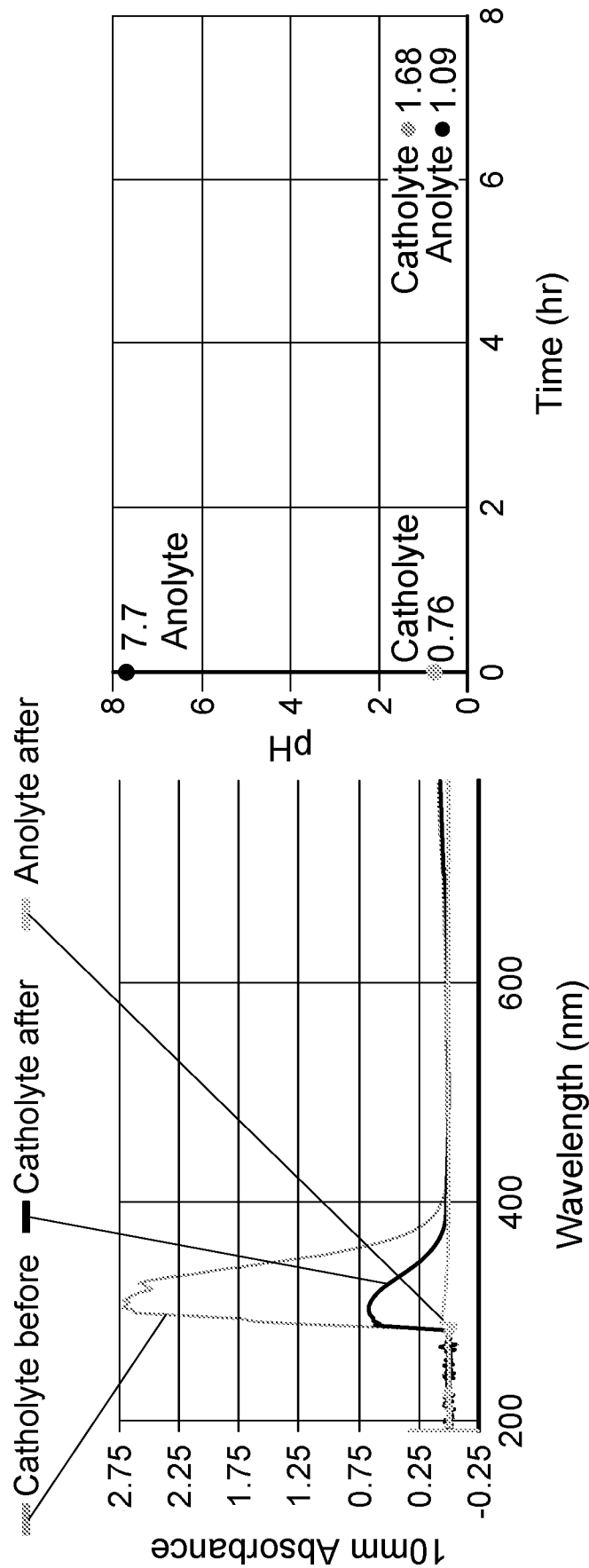


FIG. 22A

FIG. 22B

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/036770

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C02F1/461	C02F1/469	C02F1/66		
ADD.	C02F101/10	C02F101/20	C02F101/22	C02F101/34	C02F103/08
	C02F103/10	C02F103/16	C02F103/18		
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols) C02F					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched					
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages				Relevant to claim No.
X	CN 115 974 116 A (SUZHOU JINQU ENVIRONMENTAL PROTECTION TECH CO LTD) 18 April 2023 (2023-04-18) paragraphs [0001], [0005] - [0035] claims 1-9 -----				1, 3 - 6, 8, 11 - 14, 17, 18, 24 - 37
X	JP 2001 073172 A (MITSUI MINING & SMELTING CO) 21 March 2001 (2001-03-21) paragraphs [0004] - [0010] ----- - / - -				1, 3 - 6, 8, 11 - 14, 17, 18, 24 - 37
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.					
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family					
Date of the actual completion of the international search 7 August 2024			Date of mailing of the international search report 15/10/2024		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Rozanska, Agnieszka		

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/036770

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2022/185708 A1 (THOMPSON-BREWSTER EMMA [AU]) 16 June 2022 (2022-06-16) figures 1-3 claims 1-21 paragraphs [0001], [0013] - [0204] -----	8,11-14, 17,18, 24-37
X	US 2019/309427 A1 (JAMES PATRICK ISMAIL [US]) 10 October 2019 (2019-10-10) figures 1-3 paragraphs [0002], [0009] - [0067] -----	8,11-14, 17,18, 24-37
X	US 2012/156126 A1 (BLUNN ADAM JUSTIN [AU] ET AL) 21 June 2012 (2012-06-21) paragraphs [0003] - [0029] -----	8,11-14, 17,18, 24-37
X	WO 2014/007033 A1 (HITACHI LTD [JP]) 9 January 2014 (2014-01-09) figures 1,2,11 paragraphs [0001], [0015] - [0046] -----	28-37

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/036770

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims;; it is covered by claims Nos.:
1, 6, 8 (completely); 3-5, 11-14, 17, 18
24-37 (partially) -----

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1, 6, 8(completely); 3-5, 11-14, 17, 18, 24-37(partially)

A method of reducing chemical content in acidic mine waste comprising contacting the acidic mine waste with an electrolyzer (in particular after contacting the acidic mine waste with a base) to form (i) a base, metal hydroxides, a product comprising insoluble salts of one or more target ions, or metallic deposition on the cathode of one or more target ions, and (ii) an acid.

2. claims: 2, 7(completely); 3-5, 11-18, 24-37(partially)

A method of reducing chemical content in acidic mine waste comprising contacting the acidic mine waste with a base and carbon dioxide to form (i) insoluble carbonate salts of one or more target ions; and (ii) a solution rich in ions; and contacting the solution rich in ions of step (a)(ii) with an electrolyzer to regenerate (i) a base and (ii) an acid.

3. claims: 9, 10, 19-23(completely); 11-18, 24-37(partially)

A method of reducing chemical content in acidic mine waste comprising contacting the acidic mine waste comprising one or more target ions with a base (in particular in an electrochemical cell) and regenerating the base in an electrochemical cell and forming therein an acidic product comprising the one or more ions.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2024/036770

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 115974116	A	18-04-2023	NONE	
JP 2001073172	A	21-03-2001	NONE	
US 2022185708	A1	16-06-2022	AU 2020247829 A1 CA 3130964 A1 CL 2021002453 A1 US 2022185708 A1 WO 2020191439 A1 ZA 202107771 B	11-11-2021 01-10-2020 22-04-2022 16-06-2022 01-10-2020 21-12-2022
US 2019309427	A1	10-10-2019	NONE	
US 2012156126	A1	21-06-2012	AP 2892 A AU 2010206486 A1 BR PI1006938 A2 CA 2750135 A1 CL 2011001762 A1 CN 102388168 A EA 201170964 A1 EP 2389461 A1 PE 20120612 A1 US 2012156126 A1 WO 2010083555 A1	31-05-2014 08-09-2011 12-04-2016 29-07-2010 24-02-2012 21-03-2012 30-03-2012 30-11-2011 23-05-2012 21-06-2012 29-07-2010
WO 2014007033	A1	09-01-2014	JP 2014014743 A WO 2014007033 A1	30-01-2014 09-01-2014