INTEGRATION OF CARBON SEQUESTRATION WITH SELECTIVE HYDROMETALLURGICAL RECOVERY OF METAL VALUES

FIELD

[0001] The invention is in the field of inorganic chemistry, integrating electrochemical processes with steps of hydrometallurgical value extraction and carbon dioxide capture.

BACKGROUND

[0002] Technologies for efficient sequestration of gaseous carbon dioxide are potentially an important tool for addressing anthropogenic climate change. Various approaches have been suggested for sequestering carbon as mineral carbonates, including techniques that accelerate weathering reactions of minerals in ultramafic and mafic source rocks. These enhanced weathering (on land) or ocean alkalinity enhancement (at sea) approaches consume CO_2 but are necessarily accompanied by a release of mineral dissolution products such as alkaline species and metal compounds, for example Si, Ca, Mg, Fe, Ni, and Co species. The ecological effect of these processes are uncertain (see Bach et al., CO_2 Removal With Enhanced Weathering and Ocean Alkalinity Enhancement: Potential Risks and Co-benefits for Marine Pelagic Ecosystems, Frontiers in Climate, vol. 1, 2019, pg 7). There is a need for processes that integrate carbon capture with the recovery of metal values from mineral feedstocks.

SUMMARY

[0003] Processes are provided in which successive steps of hydrometallurgical value extraction are carried out on a mineral feedstock, such as an olivine, mafic, saprolite or ultramafic feedstock. In select ~~embodiment~~examples, the products of carbon capture reactions and an electrolytic reagent-generating process are utilized as inputs to hydrometallurgical value recovery steps. The electrolytic process provides the acid leachant (HCl or H_2SO_4) and an alkali hydroxide (NaOH or KOH), with the alkali hydroxide then available for use either directly as a precipitant in the hydrometallurgical steps, or available for conversion to an alkali metal carbonate or bicarbonate that can in turn be used as the precipitant in the hydrometallurgical

steps. In an alternative ~~embodiment~~example, the alkali hydroxide from the chloralkali process may be used to precipitate a calcium hydroxide product, with the calcium hydroxide product then available for use directly in carbon dioxide gas scrubbing, or for use to accept a carbonate that is provided by a CO_2 scrubbing process.

[0004] Processes are accordingly provided for the coproduction from mineral feedstocks such as basaltic rocks of less carbon intensive, or carbon negative, nickel, iron, calcium and magnesium hydroxides or carbonates. Basaltic sand materials that include amorphous silicates may also be produced. These processes may involve (1) magnetic separation, (2) hydrochloric or sulfuric acid leaching, (3) selective precipitation of metal hydroxides or carbonates in successive steps, which may involve pH modulation (in select ~~embodiment~~examples, nickel may for example be separated using a resin in leach step) (4) electrolysis of a resulting barren solution, for example a chloralkali process for treating $NaCl_{(aq)}$, or an electrolytic salt splitting anion exchange process for treating $Na_2SO_{4(aq)}$, and (5) acid and alkali reagent recycling, for example in the case of a chloralkali process, hydrochloric acid production from the hydrogen and chlorine gas products of the electrolysis.

[0005] Process of the ~~invention~~disclosure accordingly provide for the use of less carbon intensive nickel, iron, calcium and magnesium hydroxides or carbonates, as well as olivine and basaltic sand material, including amorphous silicates, in marketable products. These may for example include feedstocks for battery, steel, cement, tyre, glass, aggregate, or concrete industries. Products of the present processes, such as the solid siliceous residue or iron precipitate products, may for example be subject to washing and/or alkalization. The adjustment of pH by way of alkalization (alkali addition) may improve the suitability of the final product, for example to produce a siliceous residue suitable for use as a supplementary cementitious material (SCM) in cements with improved cementitious properties.

[0006] The present processes provide avenues for the coproduction of less carbon intensive nickel and iron hydroxides, and this in turn may provide avenues to decarbonate sectors associated with the transition to a low carbon economy - such as electric vehicles and batteries. The ~~invention~~disclosure also facilitates low carbon steelmaking, by compensating carbon heavy pyrometallurgy with a carbon negative magnetic, hydrometallurgical and electrochemical process.

[0007] The present processes provide for the coproduction of less carbon intensive amorphous silicates, marketable as a supplementary cementitious material (SCM) for cements, or in the tyre manufacturing industry. Basaltic sand materials may be produced by the present processes, with an inert surface, for example for use as aggregate in concrete mixes. The ~~invention~~disclosure accordingly facilitates the construction of less carbon intensive concrete buildings.

[0008] Processes are accordingly provided for processing a comminuted mineral feedstock, comprising:

optionally magnetically separating material from the comminuted mineral feedstock;

a) leaching metal values from the comminuted mineral feedstock with an acid leachant, to produce a solid siliceous residue and a loaded leach solution;

optionally subjecting the loaded leach solution to a resin in leach process so as to selectively remove nickel and cobalt values from the loaded leach solution, to obtain a purified nickel and cobalt combined product,

optionally, washing and/or alkalization of the solid siliceous residue, for example to form a supplementary cementitious material (SCM) for use in cements;

b) precipitating iron and/or aluminum from the loaded leach solution with addition of:

a first alkali metal carbonate or bicarbonate precipitant,

to produce a carbon dioxide off gas, or,

a first alkali hydroxide precipitant,

to produce an Fe/Al depleted solution and an iron and/or aluminum hydroxide or oxide (e.g. hematite) precipitate product;

optionally, washing and/or alkalization of the iron and/or aluminum hydroxide precipitate product;

optionally, adding a hematite seed material to the step of precipitating iron and/or aluminum, wherein the iron and/or aluminum

to produce a Ni/Co depleted solution and a nickel and/or cobalt carbonate or hydroxide precipitate product, such as a mixed Ni/Co hydroxide product;

d) before or after step (c), precipitating iron and/or aluminum and/or manganese from the Ni/Co depleted solution with addition of an oxidant (such as chlorine gas ($Cl_{2(g)}$) or sodium hypochlorite (NaOCl)) and with addition of:

a third alkali metal carbonate or bicarbonate precipitant, or,

a third alkali hydroxide precipitant,

to produce an Fe/Al/Mn depleted solution and an iron and/or aluminum and/or manganese hydroxide precipitate product;

e) precipitating magnesium from the Fe/Al/Mn depleted solution with addition of:

a fourth alkali hydroxide precipitant, or

a fourth alkali metal carbonate or bicarbonate precipitant,

to produce a Mg-depleted solution and a magnesium hydroxide or carbonate precipitate product;

f) subjecting the Mg-depleted solution to an electrolysis process to produce the acid leachant and:

one or more of the alkali hydroxide precipitants, or

an alkali hydroxide product.

In one aspect, the present disclosure refers to a process for processing a comminuted nickel saprolite mineral feedstock, comprising:

a) leaching iron, aluminum, nickel, cobalt, manganese and magnesium metal values from the comminuted mineral feedstock with an HCl acid leachant, to produce a solid siliceous residue and a loaded leach solution;

b) precipitating iron and aluminum from the loaded leach solution with addition of:

a first NaOH alkali hydroxide precipitant,

to produce an Fe/Al depleted solution and an iron and/or aluminum hydroxide or oxide precipitate product;

c) precipitating nickel and cobalt from the Fe/Al depleted solution, wherein the precipitating is with addition of:

a second NaOH alkali hydroxide precipitant,

to produce a Ni/Co depleted solution and a nickel and cobalt mixed hydroxide precipitate product;

d) precipitating manganese from the Ni/Co depleted solution with addition of an oxidant and with addition of:

a third NaOH alkali hydroxide precipitant,

to produce an Fe/Al/Mn depleted solution and an manganese hydroxide precipitate product;

e) precipitating magnesium from the Fe/Al/Mn depleted solution with addition of:

a fourth NaOH alkali hydroxide precipitant,

to produce a Mg-depleted solution and a magnesium hydroxide precipitate product;

f) subjecting the Mg-depleted solution to a chloralkali process producing the NaOH alkali hydroxide precipitant, a $Cl_{2(g)}$ product and a $H_{2(g)}$ product, further comprising reacting the $Cl_{2(g)}$ product and the $H_{2(g)}$ product to produce HCl as the HCl acid leachant.

Processes may further involve reacting the alkali hydroxide product of the electrolysis process directly or indirectly with a carbon source to produce one or more of the alkali metal carbonate or bicarbonate precipitants. The step of reacting the alkali hydroxide product with a carbon source may involve scrubbing carbon dioxide from a CO_2 containing gas by treating the CO_2 containing gas with a scrubbing solution comprising the alkali hydroxide product, to produce one or more of the alkali metal carbonate or bicarbonate precipitants.

In select ~~embodiment~~examples, calcium may be precipitated from the Mg-depleted solution with a fifth alkali hydroxide precipitant, to produce a calcium hydroxide

product, and generating one or more of the alkali metal carbonate or bicarbonate precipitants by treating the calcium hydroxide product with a carbon source, such as a CO_2 containing gas or a metal carbonate, and the CO_2 containing gas may for example be air. When the alkali hydroxide product comprises NaOH, scrubbing carbon dioxide from the CO_2 containing gas may accordingly involve precipitating Na_2CO_3 hydrates from the scrubbing solution in a crystallisation process to produce a solid Na_2CO_3 crystallizer product, and one or more of the alkali metal carbonate or bicarbonate precipitants comprises the solid Na_2CO_3 crystallizer product.

In alternative ~~embodiment~~examples, the alkali metal carbonate or bicarbonate precipitant may be one or more of $NaHCO_3$, Na_2CO_3 or K_2CO_3, or a mixture thereof. The alkali hydroxide precipitant may be one or both of NaOH or KOH, or a mixture thereof. The acid leachant may for example be a mineral acid, such as HCl or H_2SO_4, or a mixture thereof.

The electrolysis process may involve a chloralkali process, producing the alkali hydroxide precipitant and/or the alkali hydroxide product, a $Cl_{2(g)}$ product and a $H_{2(g)}$ product. The $Cl_{2(g)}$ product and the $H_{2(g)}$ product may then be reacted to produce HCl as the acid leachant.

When the Mg-depleted solution includes Na_2SO_4, the electrolysis process may involve a salt splitting process that includes electrolytic generation of: the alkali hydroxide product and/or the alkali hydroxide precipitant; and, H_2SO_4 as the acid leachant.

Precipitating magnesium from the Fe/Al/Mn depleted solution with the alkali hydroxide precipitant, may involve addition of a $CO_{2(g)}$ precipitant to produce the Mg-depleted solution and the magnesium carbonate precipitate product. The $CO_{2(g)}$ precipitant may for example include, or be made entirely from, the carbon dioxide off gas from the step of precipitating iron and/or aluminum from the loaded leach solution.

In select ~~embodiment~~examples, an initial step of magnetically separating material from the comminuted mineral feedstock may be implements, for example so as to enrich the feedstock in select materials.

In select ~~embodiment~~examples, the loaded leach solution may be subjected to a resin in leach process so as to selectively remove nickel values from the loaded leach solution, to obtain a purified nickel product.

The products of the process may be further treated for example by washing and/or alkalization of the solid siliceous residue, washing and/or alkalization of the iron and/or aluminum hydroxide or oxide precipitate product.

A hematite seed material may be added to the step of precipitating iron and/or aluminum so as to seed the precipitation of a hematite product. When the iron and/or aluminum hydroxide or oxide precipitate product comprises a hematite seed material, the hematite seed material may be recirculated to the step of precipitating iron and/or aluminum so as to seed the precipitation of a hematite product.

A brine that includes some or all of the Fe/Al/Mn depleted solution may be recirculated to the comminuting step, to provide the comminuted mineral feedstock.

The mineral feedstock may for example be, or include, one or more of a nickel saprolite ore or tailing, an olivine ore or tailing, an asbestos ore or tailing, a mafic mineral, a saprolite material, an ultramafic rock, olivine, wollastonite or combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] **Figure 1** is a schematic illustration of an integrated process for hydrometallurgical value extraction from a mineral feedstock, with reactants for the hydrometallurgical process provided by capture of carbon dioxide and a chloralkali electrochemical process.

[0010] **Figure 2** is a schematic illustration of an integrated process for hydrometallurgical value extraction from a mineral feedstock, with reactants for the hydrometallurgical process provided by capture of carbon dioxide and a chloralkali electrochemical process.

[0011] **Figure 3** is a schematic illustration of an integrated process for hydrometallurgical value extraction from a mineral feedstock, with reactants for the

CLAIMS

1. A process for processing a comminuted nickel saprolite mineral feedstock, comprising:

a) leaching iron, aluminum, nickel, cobalt, manganese and magnesium metal values from the comminuted mineral feedstock with an HCl acid leachant, to produce a solid siliceous residue and a loaded leach solution;

b) precipitating iron and~~/or~~ aluminum from the loaded leach solution with addition of:

~~a first alkali metal carbonate precipitant, to produce a carbon dioxide off gas, or,~~

a first NaOH alkali hydroxide precipitant,

to produce an Fe/Al depleted solution and an iron and/or aluminum hydroxide or oxide precipitate product;

c) precipitating nickel and~~/or~~ cobalt from the Fe/Al depleted solution ~~or from a Ni/Co ion exchange eluant obtained from the Fe/Al depleted solution by selective extraction of nickel and/or cobalt on an ion exchange medium~~, wherein the precipitating is with addition of:

~~a second alkali metal carbonate or bicarbonate precipitant, or,~~

a second NaOH alkali hydroxide precipitant,

to produce a Ni/Co depleted solution and a nickel and~~/or~~ cobalt ~~carbonate or~~ mixed hydroxide precipitate product;

d) ~~before or after step (c),~~ precipitating ~~iron and/or aluminum and/or~~ manganese from the Ni/Co depleted solution with addition of an oxidant and with addition of:

~~a third alkali metal carbonate or bicarbonate precipitant, or,~~

a third NaOH alkali hydroxide precipitant,

to produce an Fe/Al/Mn depleted solution and an ~~iron and/or aluminum and/or~~ manganese hydroxide precipitate product;

e) precipitating magnesium from the Fe/Al/Mn depleted solution with addition of:

a fourth NaOH alkali hydroxide precipitant, ~~or~~

~~a fourth alkali metal carbonate or bicarbonate precipitant,~~

to produce a Mg-depleted solution and a magnesium hydroxide ~~or carbonate~~ precipitate product;

f) subjecting the Mg-depleted solution to ~~an electrolysis process to produce the acid leachant and:~~

~~one or more of the alkali hydroxide precipitants~~a chloralkali process producing the NaOH alkali hydroxide precipitant, a $Cl_{2(g)}$ product and a $H_{2(g)}$ product, further comprising reacting the $Cl_{2(g)}$ product and the $H_{2(g)}$ product to produce HCl as the HCl acid leachant~~, or~~

~~an alkali hydroxide product~~.

~~2. The process of claim 1, further comprising reacting the alkali hydroxide product of the electrolysis process directly or indirectly with a carbon source to produce one or more of the alkali metal carbonate or bicarbonate precipitants.~~

~~3~~2. The process of claim ~~2~~1, ~~wherein~~ further comprising reacting the NaOH alkali hydroxide product of the electrolysis process with ~~a carbon source comprises scrubbing carbon dioxide from~~ a CO_2 containing gas ~~by treating the CO_2 containing gas with a scrubbing solution comprising the alkali hydroxide product~~, thereby scrubbing carbon dioxide from the CO_2 containing gas to produce ~~one or more of the alkali metal carbonate or bicarbonate precipitants~~ an alkali metal carbonate or bicarbonate comprising $NaHCO_3$ or Na_2CO_3.

~~4~~3. The process of claim ~~3~~2, ~~wherein the alkali hydroxide product comprises NaOH,~~ wherein scrubbing carbon dioxide from the CO_2 containing gas

comprises precipitating Na_2CO_3 hydrates from the scrubbing solution in a crystallisation process to produce a solid Na_2CO_3 crystallizer product.

~~5. The process of any one of claims 1-4, further comprising precipitating calcium from the Mg-depleted solution with a fifth alkali hydroxide precipitant, to produce a calcium hydroxide product, and generating one or more of the alkali metal carbonate or bicarbonate precipitants by treating the calcium hydroxide product with a carbon source.~~

~~6. The process of claim 5, wherein the carbon source is a CO_2 containing gas or a metal carbonate.~~

~~7. The process of claim 3, 4 or 6, wherein the CO_2 containing gas comprises air.~~

~~8. The process of claim 4, wherein one or more of the alkali metal carbonate or bicarbonate precipitants comprises the solid Na_2CO_3 crystallizer product.~~

~~9. The process of any of claims 1-8, wherein the alkali metal carbonate or bicarbonate precipitant comprises $NaHCO_3$, Na_2CO_3 or K_2CO_3.~~

~~10. The process of any one of claims 1-9, wherein the alkali hydroxide precipitant comprises NaOH or KOH.~~

~~11. The process of any one of claims 1-10, wherein the acid leachant comprises a mineral acid, HCl or H_2SO_4.~~

~~12. The process of any one of claims 1-11, wherein the electrolysis process comprises a chloralkali process producing the alkali hydroxide precipitant and/or the alkali hydroxide product, a $Cl_{2(g)}$ product and a $H_{2(g)}$ product, further~~

~~comprising reacting the $Cl_{2(g)}$ product and the $H_{2(g)}$ product to produce HCl as the acid leachant.~~

~~13. The process of any one of claims 1-11, wherein the Mg-depleted solution comprises Na_2SO_4, wherein the electrolysis process comprises a salt splitting process comprising electrolytic generation of: the alkali hydroxide product and/or the alkali hydroxide precipitant; and, H_2SO_4 as the acid leachant.~~

~~14. The process of any one of claims 1-13, wherein precipitating magnesium from the Fe/Al/Mn depleted solution with the alkali hydroxide precipitant, further comprises addition of a $CO_{2(g)}$ precipitant to produce the Mg-depleted solution and the magnesium carbonate precipitate product.~~

~~15. The process of claim 14, wherein the $CO_{2(g)}$ precipitant comprises the carbon dioxide off gas from the step of precipitating iron and/or aluminum from the loaded leach solution.~~

~~16~~4. The process of any one of claims 1-~~15~~3, wherein the oxidant comprises chlorine gas ($Cl_{2(g)}$) or sodium hypochlorite (NaOCl).

~~17. The process of any one of claims 1-16, wherein the nickel and/or cobalt hydroxide precipitate is a mixed Ni/Co hydroxide product.~~

~~18~~5. The process of any one of claims 1-~~17~~4, further comprising magnetically separating material from the comminuted mineral feedstock.

~~19~~6. The process of any one of claims 1-~~18~~5, further comprising subjecting the loaded leach solution to a resin in leach process so as to selectively remove nickel values from the loaded leach solution, to obtain a purified nickel product.

~~20~~7. The process of any one of claims 1-~~19~~6, further comprising washing and/or alkalization of the solid siliceous residue.

~~21~~8. The process of any one of claims 1-~~20~~7, further comprising washing and/or alkalization of the iron and/or aluminum hydroxide or oxide precipitate product.

~~22~~9. The process of any one of claims 1-~~21~~8, further comprising adding a hematite seed material to the step of precipitating iron and~~/or~~ aluminum so as to seed the precipitation of a hematite product.

~~23~~10. The process of any one of claims 1-~~21~~8, wherein the iron and/or aluminum hydroxide or oxide precipitate product comprises a hematite seed material, and the hematite seed material is recirculated to the step of precipitating iron and/or aluminum so as to seed the precipitation of a hematite product.

~~24~~11. The process of any one of claims 1-~~23~~10, further comprising recycling a brine comprising the Fe/Al/Mn depleted solution to a comminuting step to provide the comminuted mineral feedstock.

~~25. The process of any one of claims 1-24, wherein the mineral feedstock comprises a nickel saprolite ore or tailing, an olivine ore or tailing, an asbestos ore or tailing, a mafic mineral, a saprolite material, an ultramafic rock, olivine or wollastonite.~~

~~25. A process for processing a comminuted mineral feedstock, comprising:~~

~~optionally magnetically separating material from the comminuted mineral feedstock;~~

~~a) leaching metal values from the comminuted mineral feedstock with an acid leachant, to produce a solid siliceous residue and a loaded leach solution;~~

~~optionally subjecting the loaded leach solution to a resin in leach process so as to selectively remove nickel values from the loaded leach solution, to obtain a purified nickel product,~~

~~optionally, washing and/or alkalization of the solid siliceous residue;~~

~~b) precipitating iron and/or aluminum from the loaded leach solution with addition of:~~

~~a first alkali metal carbonate or bicarbonate precipitant, to produce a carbon dioxide off gas, or,~~

~~a first alkali hydroxide precipitant,~~

~~to produce an Fe/Al depleted solution and an iron and/or aluminum hydroxide or oxide precipitate product, optionally a hematite product;~~

~~optionally, washing and/or alkalization of the iron and/or aluminum hydroxide precipitate product;~~

~~optionally, adding a hematite seed material to the step of precipitating iron and/or aluminum, and further optionally wherein the iron and/or aluminum hydroxide or oxide precipitate product comprises the hematite seed material;~~

~~c) precipitating nickel and/or cobalt from the Fe/Al depleted solution or from a Ni/Co ion exchange eluant obtained from the Fe/Al depleted solution by selective extraction of Ni and/or cobalt on an ion exchange medium, wherein the precipitating is with addition of:~~

~~a second alkali metal carbonate or bicarbonate precipitant, or,~~

~~a second alkali hydroxide precipitant,~~

~~to produce a Ni/Co depleted solution and a nickel and/or cobalt carbonate or hydroxide precipitate product;~~

~~d) before or after step (c), precipitating iron and/or aluminum and/or manganese from the Ni/Co depleted solution with addition of an oxidant and with addition of:~~

~~a third alkali metal carbonate or bicarbonate precipitant, or,~~

~~a third alkali hydroxide precipitant,~~

~~to produce an Fe/Al/Mn depleted solution and an iron and/or aluminum and/or manganese hydroxide precipitate product;~~

~~optionally recycling a brine comprising the Fe/Al/Mn depleted solution to a comminuting step to provide the comminuted mineral feedstock;~~

~~e) precipitating magnesium from the Fe/Al/Mn depleted solution with addition of:~~

~~a fourth alkali hydroxide precipitant, or~~

~~a fourth alkali metal carbonate or bicarbonate precipitant,~~

~~to produce a Mg-depleted solution and a magnesium hydroxide or carbonate precipitate product;~~

~~f) subjecting the Mg-depleted solution to an electrolysis process to produce the acid leachant and:~~

~~one or more of the alkali hydroxide precipitants, or~~

~~an alkali hydroxide product; and,~~

~~g) sequestering carbon dioxide from a CO_2 containing gas, by reacting the CO_2 containing gas directly or indirectly with the alkali hydroxide product, in one or more of: the nickel and/or cobalt carbonate precipitate product; or, the magnesium carbonate precipitate product.~~