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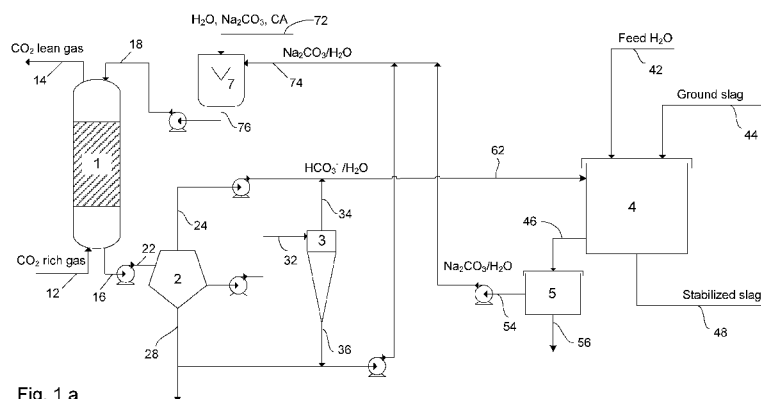


Fig. 1 a

(57) Abstract: Methods and processes for stabilizing a ground slag produced from a steelmaking operation. Optionally, a CO₂-containing gas may be contacted with an aqueous absorption solution in presence of a biocatalyst, in a reactor, for enzymatically catalyzing a hydration reaction of dissolved CO₂ into bicarbonate ions and hydrogen ions to produce an ion loaded solution and a CO₂ lean gas. The ion loaded solution is then contacted with the ground slag to produce CaCO₃, MgCO₃, a stabilized slag depleted in CaO and MgO, and an alkaline liquor comprising carbonate ions CO₃²⁻. Alternatively, the ground slag may be contacted with water to leach CaO and MgO and produce a slurry containing Ca(OH)₂ and Mg(OH)₂, which is contacted with the ion loaded solution to produce CaCO₃ and MgCO₃ and the stabilized slag depleted in CaO and MgO.

SLAG STABILIZATION WITH CAPTURED CARBON DIOXIDE**FIELD OF THE INVENTION**

The present invention generally relates to the field of steelmaking and gaseous CO₂ capture. More particularly, the present invention concerns processes for capturing CO₂ from steelmaking operations using carbonate/bicarbonate based absorption in combination with biocatalysts.

BACKGROUND OF THE INVENTION

CO₂ emissions from a steelmaking process are about twice the amount of the steel produced. In 2005, global steel industry with a production of 1147 Mt emitted 2200 to 2500 Mt CO₂, including emissions from coke manufacture and indirect emissions due to power consumption. While in 2010, the worldwide steel production was increased to 1414 Mt (www.worldsteel.org). The CO₂ emitted from the iron and steel industry was around 2830 Mt, which is about 7% of global CO₂ emissions.

Slag is a byproduct from iron and steel making processes. It includes calcium silicates and ferrites combined with oxides of iron, aluminum, manganese, calcium, and magnesium, as shown in Table 1.

Table 1: Main chemical components and physical properties of steelmaking slags

Composition (wt%)	BOF	EAF	LMF
CaO	40.9	35.9	50.0
SiO ₂	12.9	9.9	4.3
FeO	21.7	28.0	6.3
MgO	12.0	10.1	4.5
Al ₂ O ₃	5.2	9.2	32.3
MnO	4.7	4.3	0.9
ρ (kg/m ³)	3614	3822	3069

BOF: Basic Oxygen Furnace, EAF: Electric Arc Furnace, LMF: Ladle Metallurgy Furnace Process.

Iron and steel slags are formed through the addition of fluxing agents such as limestone or dolomite to blast furnaces and steel furnaces to strip the impurities from iron ore, steel scrap, and other ferrous feeds. After cooling down to ambient temperature, the slags are processed similar to bulk aggregate through sizing, separation and transport. Slag processing typically consists of crushing, screening, and magnetic separation. The magnetically recovered slag may be returned to the blast and steel furnaces as ferrous and flux feed. Up to 50% of the slag volume is recovered as magnetic for return to the furnace. The nonmagnetic materials of the slags are graded by size, and stockpiled for sale.

Slags are a mix of iron and other steelmaking wastes (see table 1). Magnetic separation is used to recover the Fe containing components of the slag. The amount of remaining nonmagnetic slags is massive and its storage causes land space occupation when landfilling is chosen.

Otherwise, slags can be mainly used in building and road constructions. An estimated 15 million tons of iron and steel slags, valued at about \$290 million, were sold in 2010 in the United States. It is estimated that annual world iron slag output in 2010 was around 230 to 270 million tons, and steel slag about 120 to 180 million tons.

Application of slags as construction materials has been around for decades such as concrete products, road bases and surfaces, and railroad ballast. Other applications are seen as:

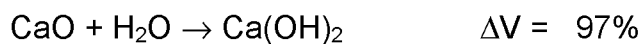
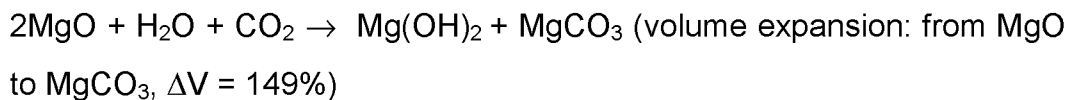
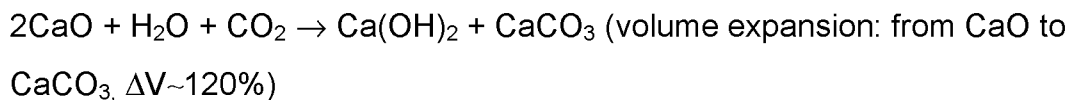
- 10 1. Iron and flux materials into blast furnace operation
2. High quality mineral aggregates
3. Portland cement
4. Unconfined construction applications
5. Soil conditioning
6. Environmental pH neutralization of abandoned mines and
 contaminated sites
7. Roofing granules and mineral wool etc.

20 The use of iron and steel slags as high quality mineral aggregates (asphaltic concrete, road base and surfaces) accounts for 63% of the steel slag sold. The next largest use is unconfined construction (fill), accounting for approximately 12-13%.

Slags contain a large amount of basic components inside the nonmagnetic slag materials such as CaO and MgO. When these basic components are in contact with moisture from surrounding air and/or water, alkaline chemicals can be leached out, causing environmental concerns related to land, in the underground water and ecosystems.

As aforesaid, slags have many applications in the constructions field. However, slag main active components, CaO and MgO, may cause material swelling, expansion and construction damages. To avoid this problem, slag can be aged or the active components can be pretreated before use. Slags then often go through an ageing period to reach stabilization. During ageing, CaO/MgO phases in the slag react with water and carbon dioxide from the air to form hydroxides and carbonates. Formation of these compounds will result in a volume change and expansion (swelling) of the slag as evidenced by the following chemical reactions and volume changes.

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20 The actual reaction kinetics of such reaction is quite slow, and full equilibrium may not be reached at atmospheric conditions before 3-6 months. Slag swelling is a concern when the slag is used as construction aggregates, thus some states in US require steelmaking slag to be stabilized in stockpiles for at least three to six months prior to use.

Slag treatments with CO₂

Apart from construction and other slag applications, one of the most attractive utilizations of iron and steel slags is the reduction of CO₂ emissions. CO₂ capture and sequestration by using iron and steel industry wastes (slags) has been

recognized recently because of slags' high concentration of alkaline components and significant CO₂ capture potential. Both CaO and MgO readily form carbonates upon contact and reaction with CO₂, while other major compounds of the slag (SiO₂, FeO/Fe₂O₃, Al₂O₃, and MnO) are inert to spontaneous reactions with carbon dioxide.

Carbonation of steel slag offers an opportunity to reduce CO₂ emissions and at the same time recycle an industrial waste.

- 10 The CO₂ capture capacity of iron and steel slag could be around 400 kg CO₂ (109 kg carbon equiv.)/ton slag, depending on the metal being processed, the type of the furnace and the post-processing treatment, which can affect not only the chemical composition, but the crystallinity, phase development, and surface morphology. For example, the blast furnace slag shows a CO₂ capture capacity in a range of 170- 450 kg CO₂/ton slag. The total sequestration potential of steelmaking slag is about 6-11% of the carbon dioxide emitted from integrated mills, and 35-45% from scrap-based steelmakers.

- 20 As the steel slag is a consolidated mixture of many compounds that are present under various phases (Table 1), different processes have been explored either through physical methods such as grinding, high temperature and pressure treatment of the slag to better expose and release the active CaO and MgO components of the slag or through chemical ways such as adding acetic acid, some other acids or different additives.

Huijgen et al (W. J. J. Huijgen, G. Witkamp, and R. N. J. Comans. Mineral CO₂ Sequestration by Slag Carbonation, *Environ. Sci. Technol.* 2005, 39, 9676-9682) investigated the possibility of capture and sequestration of CO₂ by using steel slags at high temperature and pressure (e.g. @150°C, 20 bars). They found that

fresh steel slags contain three major phases of calcium as portlandite Ca(OH)_2 , Ca-(Fe)-silicate, and Ca-Fe-O, as well as several mineral phases including Mg-Fe-O, FeO, and trace of calcite (CaCO_3). For the CO_2 sequestration through calcium carbonation, five key process steps were identified: (1) diffusion of Ca toward the surface of the solid steel slag particles; (2) dissolution of Ca from the surface into the solution; (3) dissolution of gaseous CO_2 ; (4) conversion of dissolved $\text{CO}_2(\text{aq.})$ to the (bi)carbonate ion; and (5) precipitation of CaCO_3 . The main process variables are (1) reaction time, (2) temperature, (3) CO_2 pressure, (4) particle size, (5) stirring speed, and (6) liquid-to-solid ratio (L/S).

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US Pat. No. 7,906,086 proposes a method of mixing water with two other industrial wastes to prepare a slurry suspension as the scrubbing material for CO_2 capture and sequestration. One of the wastes was selected from cement kiln dust, lime kiln dust, clinker dust, or slaked lime, and another was the iron and steel slag. Such industrial wastes contain plenty of alkaline earth metal oxides such as CaO and MgO, which could be used for CO_2 sequestration. To have a good flow and to avoid settling of particles from the suspension, mixing and agitation of the slurry is needed; and to have a smaller particle size (the smaller the particles in size, the better the performance) of the particles in the suspension, a further processing of the suspension by milling or grinding with a ball mill is suggested. The method may have challenges, for example because mixing and agitation may be difficult when the solid content is high due to high viscosity. When further processing equipment is added, the system may be too complicated and costly, accordingly the use of slag with such a method would be limited. Further, it may be difficult to separate the formed CaCO_3 from other particles in a solid mixture form, thus the precipitated solid particles (CaCO_3) would not be used for other purposes.

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U.S. Pat. No. 7,919,064 discloses an approach for CO₂ capture by using diluted carbonate salt solutions such as Na₂CO₃ or K₂CO₃ or carbonate salts with metal ions from minerals of cement plants or the slag wastes. No detailed descriptions regarding the slag uses and mineral leaching, reaction and sequestration with the leached minerals are given. Further the absorption rate of CO₂ in the diluted carbonate salt solution would be low due to the intrinsic slow mass transfer behavior of the gaseous CO₂ into the carbonate salt system, thus the efficiency of CO₂ capture in the system would be limited. Indeed, even though carbonate solutions may exhibit numerous advantages over broadly used amine based absorption solutions such as good stability to oxygen and high temperatures, and lower energy requirements for desorption, they are characterized by a relatively low rate of CO₂ absorption which results in large capture equipment and corresponding capital costs.

In such known processes, the techniques are quite complicated or imply the use of high temperatures and pressures, or CO₂ injection directly into the reaction system in gaseous form. Disadvantages may be as follows:

- leaching method using high temperatures and pressures are not practical considering the large quantity of the produced slags. The equipment and capital cost for the high temperature and pressure system would keep it out of the market for a practical use;
- Methods where CO₂ is directly injected into a slag reactor or treating system to contact and react with the slag particles, the gaseous CO₂ has to undergo several process stages as described in Huijgen et al, e.g. diffusion and dissolution of the gaseous CO₂ into the aqueous solution and conversion of the dissolved CO₂ into the (bi)carbonate before the CO₂ reaches the surface and reacts with the slag particles. Moreover, as has been observed, calcium carbonate forms and accumulates on the surface of the slag particles, which could block

some active sites and pathways for diffusion of the calcium ions from inside of the slag particles to the surface or the (bi)carbonate ions to access and react with the Ca^{++} of the slag.

Accordingly, the carbonation rates of such processes could be considerably hindered, and the potential of the iron and steel slag for CO_2 capture and sequestration would not be achieved.

A slag sequestration system should be relatively simple, efficient and robust to allow for minimal cost impact on slag handling.

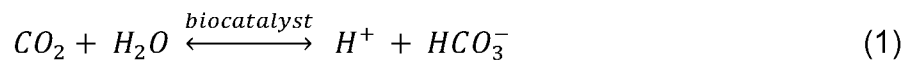
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Bonenfant et al (D. Bonenfant, L. Kharoune, S. Sauve, R. Hausler, P. Niquette, M. Mimeault, M. Kharoune. Ind. Eng. Chem. Res. 2008, 47, 7610-7616) have showed that the main mineral component of calcium in the steel slags can be leached out at ambient pressure and temperature, and the leached minerals are readily reactive for the CO_2 sequestration. Similar behaviors have been observed by Stolaroff et al (Joshuah K. Stolaroff, Gregory V. Lowry, David W. Keith, Using CaO- and MgO-rich industrial waste streams for carbon sequestration, Energy Conversion and Management, 46 (2005) 687-699), showing that $\text{Ca}(\text{OH})_2$ and CaO from steel slags or even from concrete wastes can be dissolved in water and reacted with CO_2 at ambient conditions; further, they have found that approximately half of the calcium can be dissolved within the first minute. This implies that industrial slags could be handled with a more efficient way, e.g. by leaching to release the most active components, or even with a continuous method to achieve proper stabilization of the slag and at the same time using the slag for CO_2 reduction purposes.

20

Biocatalysts have been used for CO_2 absorption applications because of their high efficiency and catalyzation. CO_2 capture and transformation enhanced by

biocatalysts (such as carbonic anhydrase (CA) enzyme or analogues) may be described as follows:



Under optimum conditions, the catalyzed turnover rate may reach 1×10^6 molecules/s, which means that one molecule of the biocatalyst, such as carbonic anhydrase or analogues, can hydrate one million molecules of carbon dioxide in a period of one second.

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There is a need for techniques that overcome at least some of the disadvantages of processes that are already known.

SUMMARY OF THE INVENTION

The present invention responds to the above need by providing processes and methods for capturing carbon dioxide, preferably from steelmaking processes, using enzymes.

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In one optional aspect of the present invention, it is provided an enzymatically enhanced method for stabilizing a ground slag produced from a steelmaking operation comprising contacting the slag with an ion loaded solution comprising bicarbonate and hydrogen ions produced from enzymatically enhanced absorption of CO_2 .

In another optional aspect of the method, the ground slag and CO_2 may be both by-products of the steelmaking operation.

In another optional aspect of the present invention, it is provided a process for conjointly stabilizing a ground slag containing CaO and MgO and absorbing CO_2 from a CO_2 -containing gas, the process comprising the steps of:

- a) contacting the CO₂-containing gas with an aqueous absorption solution in presence of a biocatalyst, in a reactor, for enzymatically catalyzing a hydration reaction of dissolved CO₂ into bicarbonate HCO₃⁻ and hydrogen ions to produce an ion loaded solution and a CO₂ lean gas;
- b) contacting the ground slag with water to leach CaO and MgO and produce a slurry containing Ca(OH)₂ and Mg(OH)₂, and
- c) contacting the slurry produced in step b) with the ion loaded solution produced in step a) to produce CaCO₃ and MgCO₃ and a slag depleted in CaO and MgO.

10 In another optional aspect of the present invention, it is provided a process for stabilizing a ground slag containing CaO and MgO, the process comprising the steps of:

- a) contacting a CO₂-containing gas with an aqueous absorption solution in presence of a biocatalyst, in a reactor, for enzymatically catalyzing a hydration reaction of dissolved CO₂ into bicarbonate HCO₃⁻ and hydrogen ions to produce an ion loaded solution and a CO₂ lean gas;
- b) desorbing CO₂ from the ion loaded solution; and
- c) contacting the ground slag containing CaO and MgO with water and the CO₂ produced in step b) to produce CaCO₃, MgCO₃ and a
20 stabilized slag depleted in CaO and MgO.

In another optional aspect of the present invention, it is provided a process for conjointly stabilizing a ground slag containing CaO and MgO and absorbing CO₂ from a CO₂-containing gas, the process comprising the steps of:

- a) contacting the CO₂-containing gas with an aqueous absorption solution in presence of a biocatalyst, in a reactor, for enzymatically catalyzing a hydration reaction of dissolved CO₂ into bicarbonate HCO₃⁻ and

hydrogen ions to produce an ion loaded solution and a CO₂ lean gas;
and

- b) contacting the ion loaded solution with the ground slag to produce CaCO₃, MgCO₃, a stabilized slag depleted in CaO and MgO, and an alkaline liquor comprising carbonate ions CO₃²⁻.

In another optional aspect, the process may further comprise the step of:

- c) recycling at least a part of carbonate ions CO₃²⁻ of the alkaline liquor produced in step b) as at least a portion of the aqueous absorption solution in the reactor of step a).

- 10 In another optional aspect, the process may further comprise mixing the ion loaded solution with water before step b) of contacting the ion loaded solution with the ground slag.

In another optional aspect of the methods or processes disclosed herein, the process may further comprise mixing the ground slag with water before step b) of contacting the ion loaded solution with the ground slag.

In another optional aspect of the methods or processes disclosed herein, the biocatalyst used may be free or immobilized biocatalyst.

In another optional aspect of the methods or processes disclosed herein, the immobilized biocatalyst may be immobilized on or in particles or as aggregates.

- 20 In another optional aspect of the methods or processes disclosed herein, the particles may be micro or nano particles.

In another optional aspect of the methods or processes disclosed herein, the biocatalyst may remain or may be fixed inside the reactor.

In another optional aspect of the methods or processes disclosed herein, the biocatalyst may flow through the reactor and may form part of the ion loaded solution.

In another optional aspect, the process may further comprise recovering the biocatalyst from the ion loaded solution before step b), and recycling at least a portion of the biocatalyst as at least a portion of the aqueous absorption solution in the reactor of step a).

In another optional aspect of the methods or processes disclosed herein, the biocatalyst may be recovered from the suspension by sedimentation, filtration and/or hydro-cyclonic separation.

In another optional aspect, the process may further comprise:

- 10 introducing the ion loaded solution containing the biocatalyst into a sedimentation separator to form a first stream rich in biocatalyst and a second stream rich in ion loaded solution having a remaining portion of biocatalyst;
- recovering the first stream at a bottom portion of the sedimentation separator and using at least a portion of the first stream as at least a portion of the aqueous absorption solution in the reactor of step a);
- recovering the second stream at a top portion of the sedimentation separator;
- filtering the second stream to form a third stream of biocatalyst and a fourth stream of ion loaded solution substantially free of biocatalyst;
- 20 recycling at least a portion of the third stream as at least a portion of the aqueous absorption solution in the reactor of step a); and
- contacting the fourth stream with the ground slag.

In another optional aspect, the step of filtering may be performed using a membrane filter allowing ultra- or micro-filtration.

In another optional aspect, the process may further comprise:

prior to step b), introducing the ion loaded solution into a sedimentation separator for separating the biocatalyst from the ion loaded solution;

recovering the biocatalyst at a bottom portion of the sedimentation separator and using at least a portion of the recovered biocatalyst as at least a portion of the aqueous absorption solution in the reactor of step a); and

recovering a primary stream comprising the ion loaded solution free of biocatalyst at a top portion of the sedimentation separator and contacting the ion loaded solution with the ground slag.

10 In another optional aspect, the process may further comprise:

recovering a secondary stream comprising remaining biocatalyst and bicarbonate ions at a mid-portion of the sedimentation separator;

introducing the secondary stream into a hydrocyclone separator for separating the remaining biocatalyst from the secondary stream;

recovering the remaining biocatalyst from the hydrocyclone separator and using at least a portion of the remaining biocatalyst as at least a portion of the aqueous absorption solution in the reactor of step a) ; and

20 recovering a tertiary stream of ion loaded solution free of biocatalyst from the hydrocyclone separator and contacting the tertiary stream with the ground slag.

In another optional aspect of the methods or processes disclosed herein, the hydrocyclone separator may comprise a plurality of hydrocyclone separators that are configured in parallel and/or in series.

In another optional aspect, the process may further comprise:

continuously conveying the slag on a conveyor;

distributing the ion loaded solution in step b) over the ground slag to produce the alkaline liquor and the stabilized slag while the ground slag is continuously conveyed on the conveyor;

separating the alkaline liquor from the stabilized slag; and

recycling at least a portion of the alkaline liquor as at least a portion of the aqueous absorption solution in the reactor of step a).

In another optional aspect, the process may further comprise:

contacting the slag with water to form a slurry comprising Ca(OH)_2 and Mg(OH)_2 , and a stabilized slag depleted in CaO and MgO ;

- 10 contacting the slurry comprising Ca(OH)_2 and Mg(OH)_2 with the ion loaded solution of step a) to produce a stream of CaCO_3 and MgCO_3 , and a stream of alkaline liquor comprising carbonate ions CO_3^{2-} ; and
- recycling at least a portion of the stream of alkaline liquor as at least a portion of the aqueous absorption solution in the reactor of step a).

In another optional aspect, the step of contacting the slag with water may further comprise:

continuously conveying the slag on a conveyor;

distributing water over the slag to form the slurry loaded in Ca(OH)_2 and Mg(OH)_2 and the stabilized slag depleted in CaO and MgO , while

20 the slag is continuously transported on the conveyor; and

introducing the slurry loaded in Ca(OH)_2 and Mg(OH)_2 into a tank where the step of contacting the slurry comprising Ca(OH)_2 and Mg(OH)_2 with the ion loaded solution of step a) is performed.

In another optional aspect of the methods or processes disclosed herein, the ion loaded solution may comprise NaHCO_3 .

In another optional aspect of the methods or processes disclosed herein, biocatalyst may be carbonic anhydrase and/or analogues thereof.

In another optional aspect of the processes disclosed herein, the ground slag and the CO₂-containing gas may be both by-products of a steelmaking operation.

In another optional aspect of the processes disclosed herein, the carbonic anhydrase may be provided free in the water; dissolved in the aqueous absorption solution; immobilized on the surface of supports that are mixed in the water and flow therewith; immobilized on the surface of supports that are fixed within the reactor; entrapped or immobilized by or in porous supports that are mixed in the water; entrapped or immobilized by or in porous supports that are fixed within the reactor; as cross-linked enzyme aggregates (CLEA); and/or as cross linked enzyme crystals (CLEC); or a combination thereof.

The present invention is an improvement in the field of CO₂ capture and sequestration. The invention involves minimal cost impact on the industrial iron and steel slag handling, and also provides opportunities to recycle such wastes for value-added applications.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1a is a process block flow diagram illustrating one embodiment of the present invention, using biocatalysts of immobilized enzymes and/or crosslinked enzyme (CLEA) microparticles and alkaline carbonate salt solutions recycled from the slag stabilization system.

Fig. 1b is a process block flow diagram illustrating another embodiment of the present invention wherein biocatalyst particles are recovered for reuse through an integrated separation process combining sedimentation and hydrocyclone separators in parallel or in series.

Fig. 2 is a process block flow diagram illustrating another embodiment of the present invention wherein biocatalysts are separated by a membrane filter system before sending the ion loaded solution to the slag stabilization process and the recovered free enzymes or the immobilized biocatalysts are recirculated into the CO₂ capture system.

Fig. 3 is a process block flow diagram illustrating another embodiment of the present invention wherein leached active components (mainly calcium hydroxide) may react with bicarbonate ions from the biocatalyst enhanced CO₂ capture process to form an industrial applicable product which can be separated from the system.

Fig. 4 is a process block flow diagram illustrating another embodiment of the present invention wherein finely ground slag is continuously transported to a conveyor system where proper containers are provided to collect the ground slag particles.

Fig. 5 is a process block flow diagram illustrating another embodiment of the present invention wherein the ground slag is continuously stabilized and recycled of the leached minerals as precipitates which can be then separated and utilized for some specific applications.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to processes for CO₂ capture and sequestration from an iron and steel production process by using steelmaking wastes (such as slag) and biocatalysts.

Biocatalysts may be carbonic anhydrase or analogues thereof. It should also be noted that "carbonic anhydrase or analogues thereof" as used herein includes naturally occurring, modified, recombinant and/or synthetic enzymes including

chemically modified enzymes, enzyme aggregates, cross-linked enzymes, enzyme particles, enzyme-polymer complexes, polypeptide fragments, enzyme-like chemicals such as small molecules mimicking the active site of carbonic anhydrase enzymes and any other functional analogue of the enzyme carbonic anhydrase.

It should be understood that carbonic anhydrase is not just a single enzyme form, but a broad group of metalloproteins that exists in three genetically unrelated families of isoforms, α , β and γ . Carbonic anhydrase (CA) is present in and may be derived from animals, plants, algae, bacteria, etc. The human variant CA II,
10 located in red blood cells, is the most studied and has a high catalytic turnover number. The carbonic anhydrase includes any analogue, fraction and variant thereof and may be alpha, gamma or beta type from human, bacterial, fungal or other organism origins, having thermostable or other stability properties, as long as the carbonic anhydrase can be provided to function in the CO₂ capture or desorption processes to enzymatically catalyse the reaction.

Regarding delivery of the enzyme to the process, in one optional aspect the enzyme is provided directly as part of a formulation or solution. There may also be enzyme provided in a reactor to react with incoming solutions and gases; for
20 instance, the enzyme may be fixed to a solid non-porous packing material, on or in a porous packing material, on or in particles or as aggregates flowing with the absorption solution within a packed tower or another type of reactor. The carbonic anhydrase may be in a free or soluble state in the formulation or immobilised on or in particles or as aggregates, chemically modified or stabilized, within the formulation. It should be noted that enzyme used in a free state may be in a pure form or may be in a mixture including impurities or additives such as other proteins, salts and other molecules coming from the enzyme production process. Immobilized enzyme free flowing in the solutions could be entrapped inside or fixed to a porous coating material that is provided around a support that

is porous or non-porous. The enzymes may be immobilised directly onto the surface of a support (porous or non porous) or may be present as cross linked enzyme aggregates (CLEAs) or cross linked enzyme crystals (CLECs). CLEA comprise precipitated enzyme molecules forming aggregates that are then cross-linked using chemical agents. The CLEA may or may not have a 'support' or 'core' made of another material which may or may not be magnetic. CLEC comprise enzyme crystals and cross linking agent and may also be associated with a 'support' or 'core' made of another material. When a support is used, it may be made of polymer, ceramic, metal(s), silica, solgel, chitosan, nylon, alumina, cellulose, alginate, polyacrylamide, magnetic particles, titanium oxide, zirconium oxide and/or other materials known in the art to be suitable for immobilization or enzyme support. When the enzymes are immobilised or provided on particles, such as micro-particles, the particles are preferably sized and provided in a particle concentration such that they are pumpable with the solution throughout the process.

CaO / MgO from steel slag waste can be dissolved in water and reacted with CO₂. They can also react with bicarbonate and such reaction could be much faster in a solution environment, especially when the gaseous CO₂ is already dissolved and converted into an aqueous form, such as the bicarbonate from the biocatalyst enhanced CO₂ capture process.

For a biocatalyst enhanced CO₂ capture process, the captured CO₂ from flue off gases is converted into a form of bicarbonate as equation (1) shows, thus such solutions are readily applicable for the CO₂ sequestration by reacting with the minerals leached out from the slag to form a permanently stable solids and such solids may be used for some other industrial applications.

Comparing to directly contacting gaseous CO₂/slag systems, the biocatalyst enhanced CO₂ capture process increases conversion of dissolved CO₂ into

(bi)carbonate ions and then CO₂ dissolution in the liquid phase. Hence the reaction or carbonation rate in such a system will be much faster, accordingly these new CO₂ sequestration systems will be more efficient.

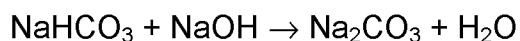
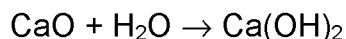
Fig. 1a presents a process flow diagram for an iron and steel slag stabilization and CO₂ capture system using biocatalysts of immobilized enzymes and/or crosslinked enzyme (CLEA) microparticles and alkaline carbonate salt solution recycled from the slag stabilization system as an aqueous absorption solution.

- 10 In an optional aspect, the aqueous absorption solution may be a carbonate-based solution, such as sodium carbonate solution, potassium carbonate solution, ammonium carbonate solution, promoted sodium carbonate solutions, promoted potassium carbonate solutions, or promoted ammonium carbonate; or any combination thereof. These carbonate-based solutions may be promoted with one or more of the above-mentioned biocatalysts.

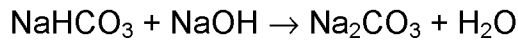
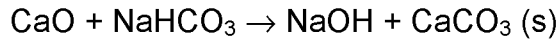
In further optional aspects of the process, the ion rich solution may contain from about 0.1 M to 10 M of bicarbonate ions. The carbonate loading of the solution will depend on the operating conditions, reactor design and the chemical
20 compounds that are added. For instance, when potassium or sodium bicarbonate compounds are used in the absorption solution, the ion rich solution may contain from about 0.2 M to 1.5 M of bicarbonate ions. When the ion rich solution is highly loaded with carbonate/bicarbonate ions, it may become much more viscous which can have a detrimental effect on mass transport within the solution. The presence of carbonic anhydrase flowing with the solution further enhances the mass transport along with the enzymatic reaction, thus improving the overall CO₂ capture, for instance by supersaturating the solution with bubbles of gaseous CO₂.

Various types of reactors may be used for the absorber, such as a packed column, a bubble column, a fluidized bed, a spray reactor, a flow wire reactor, or another type or design, preferably for gas-liquid contact.

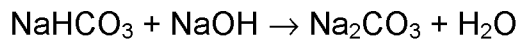
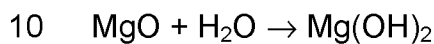
Steelmaking off gas and/or other flue gases rich in CO₂ is fed into the gas inlet port **12** near the bottom of the absorber **1**. After contact and reaction with the aqueous absorption solution (containing H₂O, Na₂CO₃, and biocatalysts inside) from the absorption solution makeup container **7**, the CO₂ from the flue gas is absorbed and converted into bicarbonate ions and collected at the bottom of the tower **16**, and further pumped into a sedimentation separator **2**, where the heavier solid particles such as the immobilized biocatalyst particles and/or aggregates are precipitated and separated from the system and collected at the bottom **28**, which can be reused or partially be removed from the system as discharge or regenerated, depending on the status of the biocatalysts being used. The less settled suspension is pumped to a hydrocyclone separator **3** which separates the remaining particles as underflow **36** and the clear part (overflow) **34** from the system. The clear aqueous solution **24** from the sedimentation separator **2**, along with the overflow part **34** from the hydrocyclone separator **3**, which are rich in bicarbonate ions (HCO₃⁻) are directed to the slag stabilization reactor or system **4**. After contacting and reacting with the ground slag particles **44** rich in active CaO and MgO, stable solids of CaCO₃ and MgCO₃ are formed and the formed solids are mixed with the slag particles. The chemical reactions during the process would be as follows:



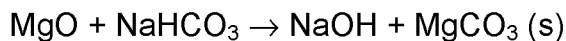
The CaO component of the slag could also directly react with the bicarbonate as follows:



Similar reactions could happen for the MgO active component:



and



Separation of the precipitated CaCO_3 and MgCO_3 particles from the system would be difficult. The performance of the stabilized slags, however, would be enhanced due to formation and addition of CaCO_3 and MgCO_3 into the slag.

Optionally, water 42 may be supplied into the stabilization system 4, for instance during the very beginning to help the leaching of the active components from the ground slag, or to adjust the concentration of the bicarbonate solution when needed.

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The stabilized slags **48** are released from the system, which may be further drained with additional processing or dewatered to recover the alkaline aqueous liquors if needed. The stabilized slags could directly be used as construction materials. The liquid phase (rich of sodium carbonate) **46** formed from the stabilization system **4** is collected in a reservoir tank **5**. Some precipitates may be formed in the tank **5**, due to settling of possible leached CaCO_3 , and MgCO_3 and

slag particles from the system, which could be removed as discharge **56** from the system.

The collected suspension **28** from the sedimentation separator **2**, and the underflow **36** from the hydrocyclone separator **3** which are rich in enzyme particles, could be reused. They may be pumped back to the absorption solution makeup system **7**. After being mixed with the clear aqueous solution **54** from the reservoir tank **5**, they are added as an aqueous absorption solution **18** into the absorber **1**. The treated steelmaking offgas **14** with less greenhouse gas CO₂ inside is discharged to the atmosphere.

The present invention provides a number of advantages. It not only takes advantages of the high efficiency of the bio-enhanced CO₂ capture technologies and advances, but provides an industrially applicable and efficient method to treat industrial iron and steel slags. Indeed, the slag stabilization and the CO₂ capture via a bio-enhanced process can be performed at ambient or low temperature and under atmospheric pressure. The present process also enables recycling of the aqueous absorption solution and biocatalysts from the suspension back to the absorber, adding efficiency to the system. Further, it comprises relatively simple apparatuses, which are relatively inexpensive to construct and maintain.

The method and apparatus disclosed herein can be tailored and retrofitted to some specific uses. Further advantages and other features will become more apparent with following embodiments and more detailed descriptions.

Fig. 1b shows a process diagram for an iron and steel slag stabilization system by using a bio-enhanced CO₂ capture technique with an aqueous absorption solution recycled from the slag stabilization system, and the biocatalyst particles could be recovered for reuse through an integrated separation process

combining sedimentation and hydrocyclone separators in parallel and series form.

In Fig. 1b, the CO₂ rich flue gas is fed into the gas inlet port **12** near the bottom of the absorber **1**. After contact and reaction with the absorption solution or suspension (containing H₂O, Na₂CO₃, and biocatalysts) from the absorption solution makeup system **7**, the CO₂ from the flue gas is absorbed and converted into bicarbonate ions and collected at the bottom of the tower **16**. The CO₂ absorbed suspension is pumped into a sedimentation separator **2**, where the heavier solid particles such as the immobilized biocatalyst particles and/or aggregates are precipitated and separated from the system and collected at the bottom **28**. The less settled suspension is pumped to a hydrocyclone separator system **3** of parallel and series hydrocyclones. The feed **32** taken from the middle layer of the sedimentation separator **2** is fed into a hydrocyclone, which separates the remaining particles as underflow **36** and the clear part (overflow) **34** from the system. To have a better recovery of the fine biocatalyst particles, the overflow from the first hydrocyclone is guided to a second hydrocyclone, and the underflow of the second hydrocyclone with rich of fine particles is recycled back to the first hydrocyclone as feed for further separation. To have a more concentrated catalyst particle suspension for recycling use, also to get more CO₂ absorbed liquor for the slag stabilization use, the underflow from the first hydrocyclone is fed into another hydrocyclone to give a dense particle suspension in the underflow **36**. The overflow from the third hydrocyclone is also recycled back to the first hydrocyclone, combined with the suspension **32** from the sedimentation separator **2** as feed to further concentrate. The clear aqueous solution **24** from the sedimentation separator **2**, along with the overflow part **34** from the second hydrocyclone separator **3**, which are rich in bicarbonate ions (HCO₃⁻) are directed to the slag stabilization reactor or system **4**. After contacting and reacting with the ground slag particles **44** rich in active CaO and MgO, stable

solids of CaCO_3 and MgCO_3 are formed and the formed solids are mixed with the slag particles. Separation of the precipitated CaCO_3 and MgCO_3 particles from the system would be difficult, while the performance of the stabilized slags would be enhanced due to formation and addition of CaCO_3 and MgCO_3 into the slag. The stabilized slags **48** are released from the system which could be directly used as construction materials. The collected suspension **28** from the sedimentation separator **2** could be partially removed from the system, which could be further regenerated for reuse. The main part of the collected suspension **28**, and the underflow **36** from the hydrocyclone system **3** rich in enzyme particles could be recirculated into the absorption system. They are pumped back to the absorption solution makeup system **7**. After being mixed with the clear aqueous solution **54** (rich of sodium carbonate) formed from the stabilization system **4** and collected in the reservoir tank **5**, they are added as aqueous absorption solution **18** into the absorber **1**. The treated steelmaking offgas **14** with less greenhouse gas CO_2 inside is discharged to the atmosphere.

Some advantages of this process are improving recovery of biocatalyst particles and providing separation apparatuses that are quite simple and easy in maintenance as compared to other separation technologies such as centrifuges and membranes.

Fig. 2 is a process flow diagram for an iron and steel slag stabilization and CO_2 capture using biocatalysts of free enzymes and/or immobilized enzymes on particles and alkaline carbonate salt solutions recycled from the slag stabilization system. The biocatalysts are separated by a membrane filter system before sending the ion loaded solution to the slag stabilization process, and the recovered free enzymes or the immobilized biocatalysts are recirculated into the CO_2 capture system.

In Fig. 2, there is shown an implementation using free enzymes or immobilized enzymes on particles such as silica, alumina or other particle supports, where the biocatalysts are separated by a membrane filter **8** which may be part of an ultrafiltration or microfiltration system, preferably ultrafiltration for the free enzymes and ultra- or microfiltration that are capable of removing fine particles from the system for the immobilized particles. The permeate **84** rich in sodium bicarbonate is sent to the slag stabilization system **4**. After contacting and reacting with the ground slag particles **44** rich in active CaO and MgO, stable solids of CaCO₃ and MgCO₃ are formed and the formed solids are mixed with the stabilized slag particles **48**. The liquid phase rich in sodium carbonate formed from the stabilization system **4** is collected in the reservoir tank **5**. Some precipitates may be formed in the tank **5**, due to settling of possible leached CaCO₃, MgCO₃ and slag particles from the system, which could be removed as discharge **56** from the system. A stream of carbonate and water **54** is pumped to the absorption solution makeup system **7**, where after being mixed with the clear aqueous solution, they are added as aqueous absorption solution **18** into the absorber **1**.

Some aggregates and heavier particles from the absorption system **1** are precipitated and collected at the bottom of the sedimentation separator **2**, which can be partially removed from the system **28**. The main part of the collected suspension **28**, and the retentate **86** from the membrane filtration system are combined and pumped back to the absorption solution makeup system **7**, via stream **74**.

Fig. 3 is a process diagram as system for stabilization of an iron and steel slag through leaching of the active components from the slag and CO₂ capture and sequestration using biocatalysts in the CO₂ capture system. The leached active components (mainly calcium hydroxide) may react with the bicarbonate ions from

the biocatalyst enhanced CO₂ capture process to form an industrial applicable product **66**, which can be separated from the system.

In Fig. 3, there is shown an implementation using water **42** to leach the active components from the slag **44** in a slag stabilization system **4**. Due to much lower (e.g. more than hundred times lower) solubility of the Mg(OH)₂ formed in the slag stabilization system **4** during the water leaching process, calcium hydroxide (Ca(OH)₂) would be the main component in the stream **47**, which is then collected in a reservoir tank **5**. Ca(OH)₂ / Mg(OH)₂ stream **64** can be pumped from the tank **5** into a reactor **6** to react with the solution **62** rich in bicarbonate ions to form calcium carbonate (and some magnesium carbonate) **66** that can be separated and collected as a product for some specific industrial applications. The alkaline liquor stream **68** rich in Na₂CO₃ is pumped from the reactor **6** back to an absorption solution makeup tank **7**, and used as the CO₂ capture aqueous absorption solution after mixing with an absorbent solution **72** and the recycled stream of the collected suspension **28** from the sedimentation separator **2** and the underflow **36** from the hydrocyclone system **3**.

There may be some unsettled calcium carbonate (CaCO₃) fine particles in stream **68** that would not have a large impact on the CO₂ capture performance and may have positive enhancement for the CO₂ absorption in the absorber, due to an increase of the gas-liquid interface surface area.

A continuous operation is illustrated on Fig.4 showing a process diagram with a roller conveyor **11** for the ground slag **44** continuous transportation while a spray system **25** for water and absorption solution spraying to stabilize the slag, collect and recycle the leached alkaline liquors **46** for CO₂ offgas capture use. The proposed system could be used either for the slag stabilization and CO₂ capture and sequestration purpose (Fig.4) and/or to recycle the precipitated CaCO₃ solids as a product (Fig.5) for some specific industrial applications.

In Fig. 4, the finely ground slag **44** is continuously transported to a conveyor system **11** where proper containers are provided to collect the ground slag particles. On top of the conveyor system **11**, water **42** and the bicarbonate solution ($\text{HCO}_3^-/\text{H}_2\text{O}$) **62** is sprayed through a spray injector **25** to leach active minerals from the fine ground slag and do the reaction between the minerals and bicarbonate ions. The chain rolling speed could be adjusted to allow for a proper leaching time and the best stabilization of the slag. The stabilized slag particles and the leached liquors are dropped into a collection system **4**, where a $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}$ stream **46** is separated and collected in the bottom, which could be used for CO_2 capture use **74**. The stabilized slag **48** could be directly used as construction materials or other purposes.

Fig. 5 shows another implementation process of continuously stabilizing the ground slag and recycling the leached minerals as precipitates which can be separated and utilized for some specific applications. On top of the conveyor system **11**, H_2O **42** is sprayed on the fine ground slag through a spray injector **27**. A stream **47** of $\text{Ca}(\text{OH})_2$ / $\text{Mg}(\text{OH})_2$ is separated from the stabilized slag collection system **4** and pumped into a reactor **6** to react with stream **62** rich of bicarbonate ions formed from the CO_2 biocatalyst enhanced capture process. During the process, precipitates of calcium carbonate (and magnesium carbonate) are produced **66**, which can be separated and collected at the bottom of the reactor **6** as a product. The liquid phase **68** from the reactor **6** with rich of Na_2CO_3 is pumped back to the absorption solution makeup tank **7**, and used as the CO_2 capture aqueous absorption solution after being mixed with the absorbent solution **72** and the recycled stream of the collected suspension **28** from the sedimentation separator **2** and the underflow **36** from the hydrocyclone system **3**.

All the processes can be operated in ambient temperature and the captured CO₂ from steelmaking off gas and/or other industrial flue gases could safely and permanently be stored in the form of stable carbonate minerals (CaCO₃ or MgCO₃).

By using slag treatment at ambient environment with water to leach out the active CaO and MgO components as Ca(OH)₂ (and some as Mg(OH)₂) water suspension, combined with the biocatalyst enhanced CO₂ capture pathway, the CO₂ emission in the steelmaking off gas is turned into a form of HCO₃⁻, after reaction with alkaline liquors (mainly Ca(OH)₂ suspension) to form stable CaCO₃ precipitates.

The method and apparatus disclosed herein can be tailored and retrofitted according to a specific situation and application. In one aspect, the present invention may relate to a process for stabilizing slags by injecting a CO₂ gas stream and water into a ground slag stabilization system. The CO₂ gas stream may be produced from desorption of an ion-rich solution including bicarbonate ions. The desorption may be performed in presence of an enzyme, such as carbonic anhydrase or analogues thereof. Optionally, the ion-rich solution may be derived from an enzymatic CO₂ capture system.

The stabilized slag product can be used directly as building and construction materials, and may have better sustainable properties. This will reduce or eliminate slag storage time and space requirements.

The solid calcium carbonate formed during the process could be separated and utilized as aggregates in the concrete industry and/or fillers in other industrial applications such polymer and paper making industries.

It is understood that above preferred embodiments are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the present invention.

CLAIMS

1. An enzymatically enhanced method for stabilizing a ground slag produced from a steelmaking operation, the method comprising contacting the ground slag with an ion loaded solution comprising bicarbonate and hydrogen ions produced from enzymatically enhanced absorption of CO₂.
2. The method of claim 1, wherein the ground slag and CO₂ are both by-products of the steelmaking operation.
3. A process for conjointly stabilizing a ground slag containing CaO and MgO and absorbing CO₂ from a CO₂-containing gas, the process comprising the steps of:
 - a) contacting the CO₂-containing gas with an aqueous absorption solution in presence of a biocatalyst, in a reactor, for enzymatically catalyzing a hydration reaction of dissolved CO₂ into bicarbonate ions and hydrogen ions to produce an ion loaded solution and a CO₂ lean gas;
 - b) contacting the ground slag with water to leach CaO and MgO and produce a slurry containing Ca(OH)₂ and Mg(OH)₂, and
 - c) contacting the slurry produced in step b) with the ion loaded solution produced in step a) to produce CaCO₃ and MgCO₃ and a slag depleted in CaO and MgO.
4. A process for stabilizing a ground slag containing CaO and MgO, the process comprising the steps of:
 - a) contacting a CO₂-containing gas with an aqueous absorption solution in presence of a biocatalyst, in a reactor, for enzymatically catalyzing a hydration reaction of dissolved CO₂ into bicarbonate ions and hydrogen ions to produce an ion loaded solution and a CO₂ lean gas;
 - b) desorbing CO₂ from the ion loaded solution; and

c) contacting the ground slag containing CaO and MgO with water and the CO₂ produced in step b) to produce CaCO₃, MgCO₃ and a stabilized slag depleted in CaO and MgO.

5. A process for conjointly stabilizing a ground slag containing CaO and MgO and absorbing CO₂ from a CO₂-containing gas, the process comprising the steps of:

a) contacting the CO₂-containing gas with a an aqueous absorption solution in presence of a biocatalyst, in a reactor, for enzymatically catalyzing a hydration reaction of dissolved CO₂ into bicarbonate ions and hydrogen ions to produce an ion loaded solution and a CO₂ lean gas; and

b) contacting the ion loaded solution with the ground slag to produce CaCO₃, MgCO₃, a stabilized slag depleted in CaO and MgO, and an alkaline liquor comprising carbonate ions CO₃²⁻.

6. The process of claim 5, comprising the step of:

c) recycling at least a part of carbonate ions CO₃²⁻ of the alkaline liquor produced in step b) as at least a portion of the aqueous absorption solution in the reactor of step a).

7. The process of claim 5 or 6, comprising mixing the ion loaded solution with water before step b) of contacting the ion loaded solution with the ground slag.

8. The process according to any one of claims 5 to 7, comprising mixing the ground slag with water before step b) of contacting the ion loaded solution with the ground slag.

9. The process according to any one of claims 5 to 8, comprising recovering the biocatalyst from the ion loaded solution before step b), and recycling at least

a portion of the biocatalyst as at least a portion of the aqueous absorption solution in the reactor of step a).

10. The process of claim 9, wherein the biocatalyst is recovered from a suspension by sedimentation, filtration and/or hydro-cyclonic separation.

11. The process of any one of claims 5 to 10, comprising:

prior to step b), introducing the ion loaded solution containing the biocatalyst into a sedimentation separator to form a first stream rich in biocatalyst and a second stream rich in ion loaded solution having a remaining portion of biocatalyst;

10 recovering the first stream at a bottom portion of the sedimentation separator and using at least a portion of the first stream as at least a portion of the aqueous absorption solution in the reactor of step a);

recovering the second stream at a top portion of the sedimentation separator;

filtering the second stream to form a third stream of biocatalyst and a fourth stream of ion loaded solution substantially free of biocatalyst;

recycling at least a portion of the third stream as at least a portion of the aqueous absorption solution in the reactor of step a); and

contacting the fourth stream with the ground slag.

20 12. The process of claim 11, wherein the filtering of the second stream is performed using a membrane filter allowing ultra- or micro-filtration.

13. The process of any one of claims 5 to 10, comprising:

prior to step b), introducing the ion loaded solution into a sedimentation separator for separating the biocatalyst from the ion loaded solution;

recovering the biocatalyst at a bottom portion of the sedimentation separator and using at least a portion of the recovered biocatalyst as at

least a portion of the aqueous absorption solution in the reactor of step a); and

recovering a primary stream comprising the ion loaded solution substantially free of biocatalyst at a top portion of the sedimentation separator and contacting the ion loaded solution with the ground slag.

14. The process of claim 13, comprising:

recovering a secondary stream comprising remaining biocatalyst and bicarbonate ions at a mid-portion of the sedimentation separator;

10 introducing the secondary stream into a hydrocyclone separator for separating the remaining biocatalyst from the secondary stream;

recovering the remaining biocatalyst from the hydrocyclone separator and using at least a portion of the remaining biocatalyst as at least a portion of the aqueous absorption solution in the reactor of step a); and

recovering a tertiary stream of ion loaded solution free of biocatalyst from the hydrocyclone separator and contacting the tertiary stream with the ground slag.

15. The process of claim 14, wherein the hydrocyclone separator comprises a plurality of hydrocyclone separators that are configured in parallel and/or in series.

20 16. The process of claim 5, comprising:

continuously conveying the ground slag on a conveyor;

distributing the ion loaded solution in step b) over the ground slag to produce the alkaline liquor and the stabilized slag while the ground slag is continuously conveyed on the conveyor;

separating the alkaline liquor from the stabilized slag; and

recycling at least a portion of the alkaline liquor as at least a portion of the aqueous absorption solution in the reactor of step a).

17. The process of claim 5, comprising:

contacting the ground slag with water to form a slurry comprising $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, and a stabilized slag depleted in CaO and MgO ;

contacting the slurry comprising $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ with the ion loaded solution of step a) to produce a stream of CaCO_3 and MgCO_3 , and a stream of alkaline liquor comprising carbonate ions CO_3^{2-} ; and

10 recycling at least a portion of the stream of alkaline liquor as at least a portion of the aqueous absorption solution in the reactor of step a).

18. The process of claim 5, wherein contacting the ground slag with water comprises:

continuously conveying the slag on a conveyor;

distributing water over the slag to form the slurry loaded in $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ and the stabilized slag depleted in CaO and MgO , while the slag is continuously transported on the conveyor; and

20 introducing the slurry loaded in $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ into a tank where contacting the slurry comprising $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ with the ion loaded solution of step a) is performed.

19. The process of any one of claims 3 to 18, wherein the ion loaded solution comprises NaHCO_3 .

20. The process of any one of claims 3 to 19, wherein the biocatalyst is carbonic anhydrase or analogues thereof.

21. The process according to any one of claims 3 to 20, wherein the biocatalyst is free or immobilized biocatalyst.

22. The process of claim 21, wherein the immobilized biocatalyst is immobilized on or in particles or as aggregates.
23. The process of claim 22, wherein the particles are micro or nano particles.
24. The process of any one of claims 3 to 23, wherein the biocatalyst remains or is fixed inside the reactor.
25. The process of any one of claims 3 to 23, wherein the biocatalyst flows through the reactor and forms part of the ion loaded solution.
26. The process of claim 3 to 25, wherein the ground slag and the CO₂-containing gas are both by-products of a steelmaking operation.
- 10 27. The process of claim 20, wherein the carbonic anhydrase is provided free in the water; dissolved in the aqueous absorption solution; immobilized on the surface of supports that are mixed in the water and flow therewith; immobilized on the surface of supports that are fixed within the reactor; entrapped or immobilized by or in porous supports that are mixed in the water; entrapped or immobilized by or in porous supports that are fixed within the reactor; as cross-linked enzyme aggregates (CLEA); and/or as cross linked enzyme crystals (CLEC); or a combination thereof.

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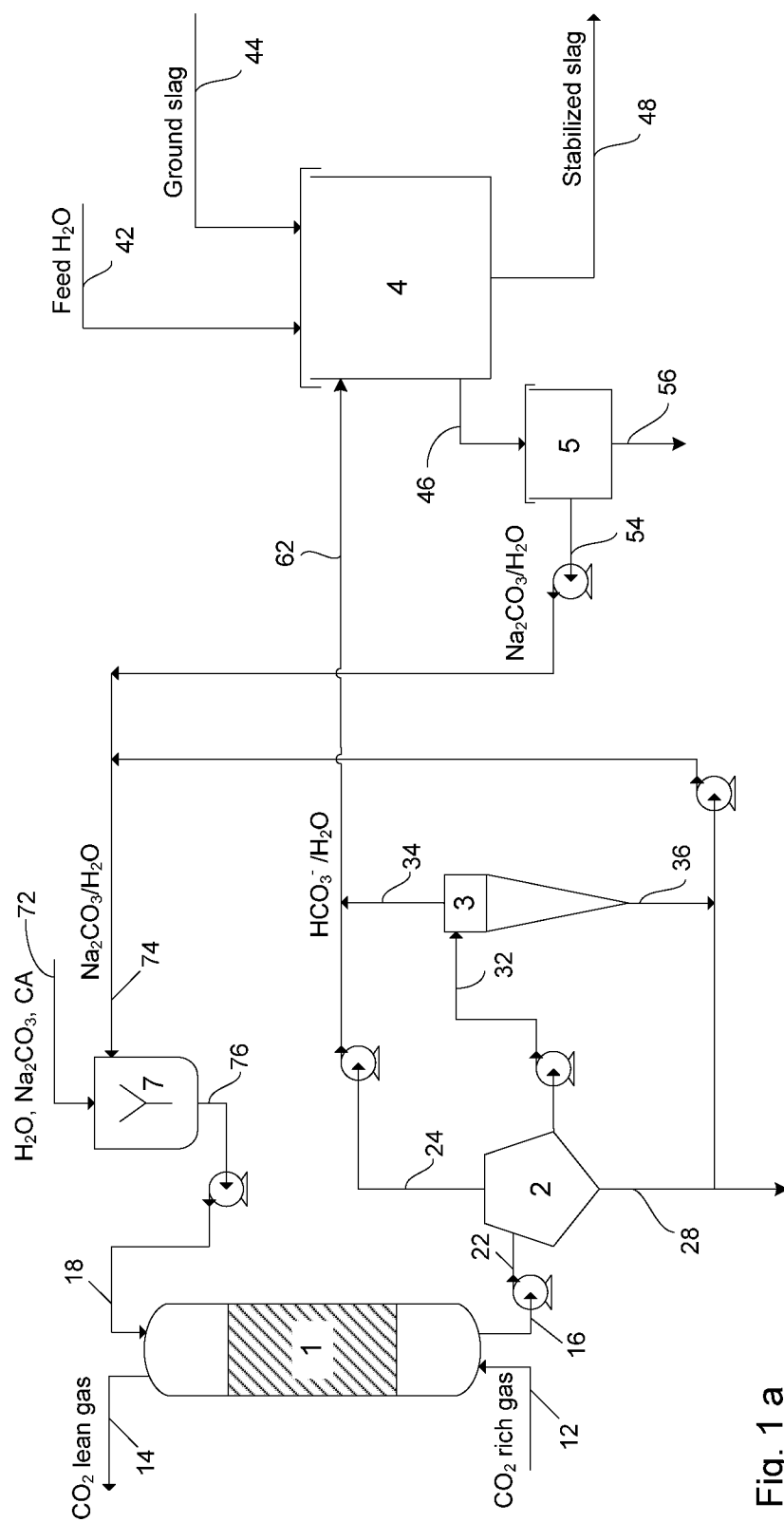


Fig. 1 a

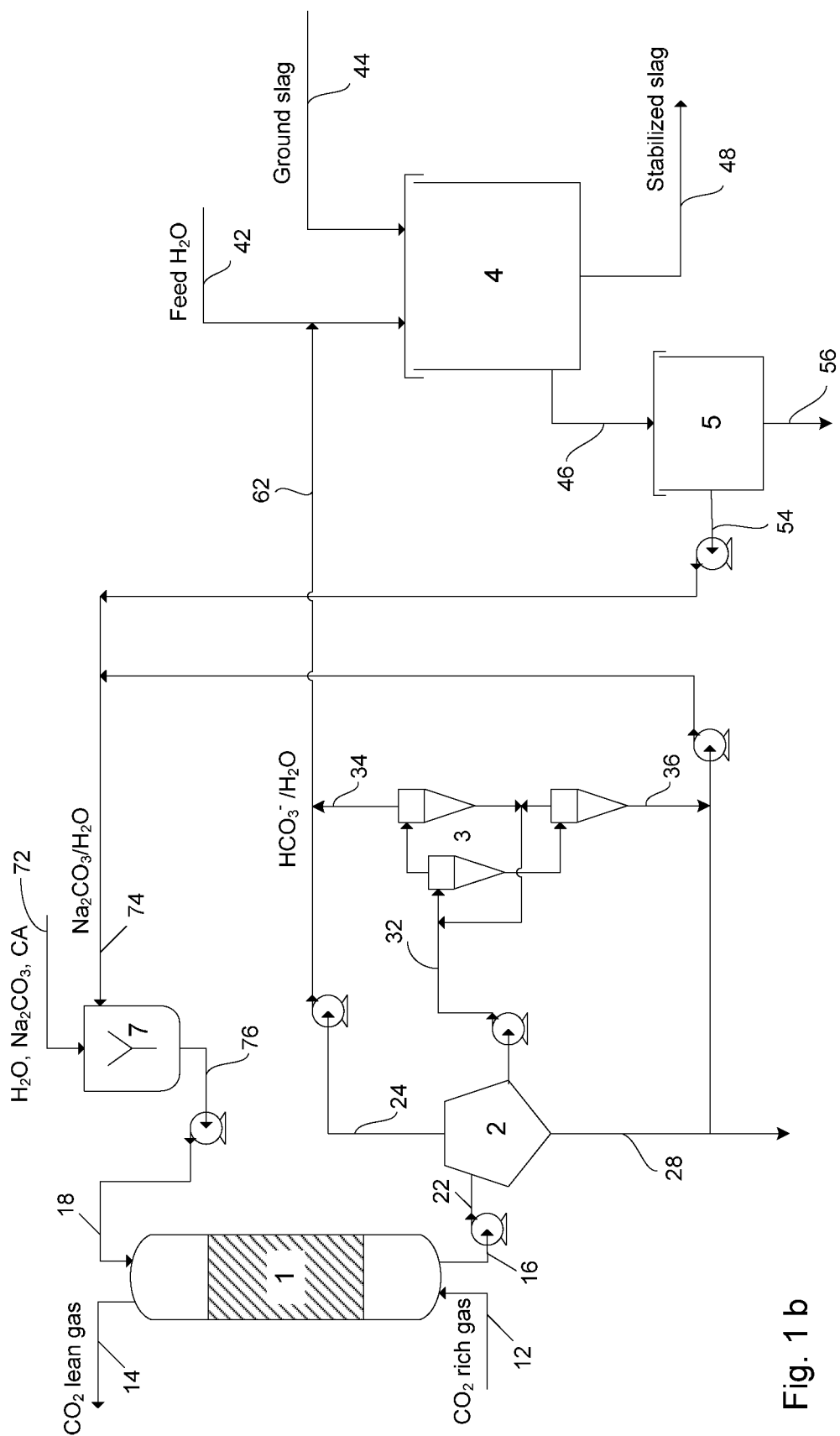


Fig. 1 b

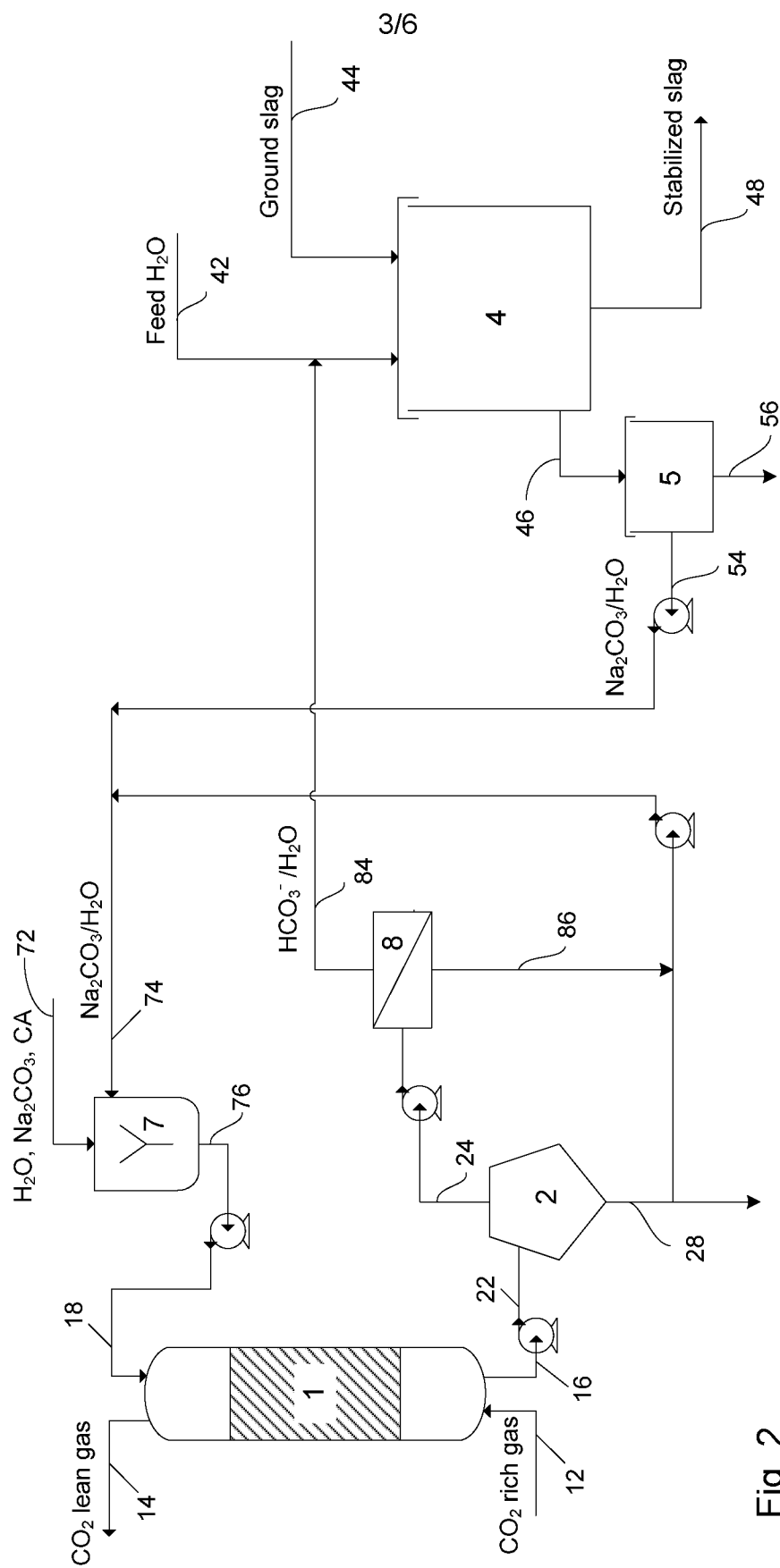


Fig. 2

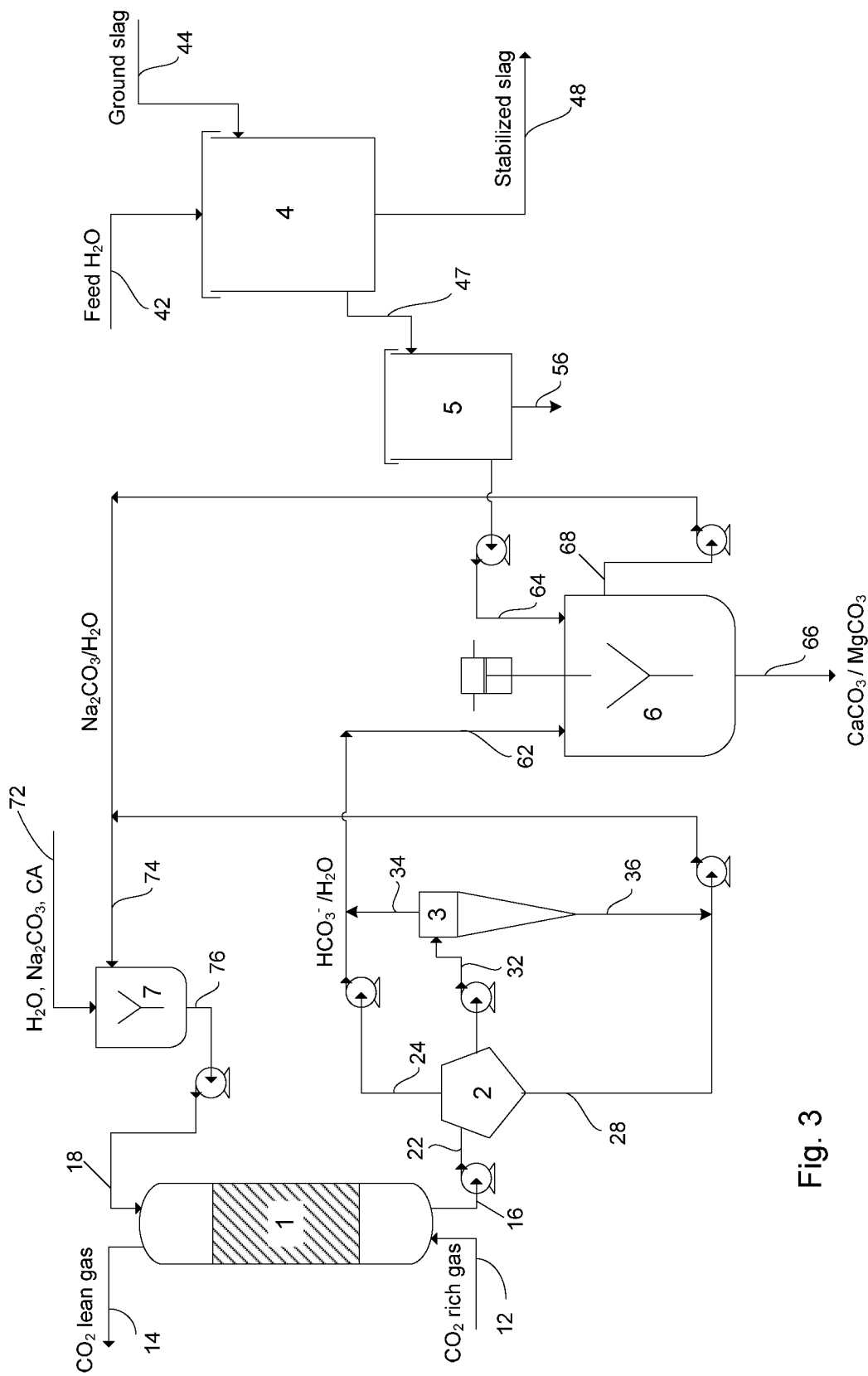


Fig. 3

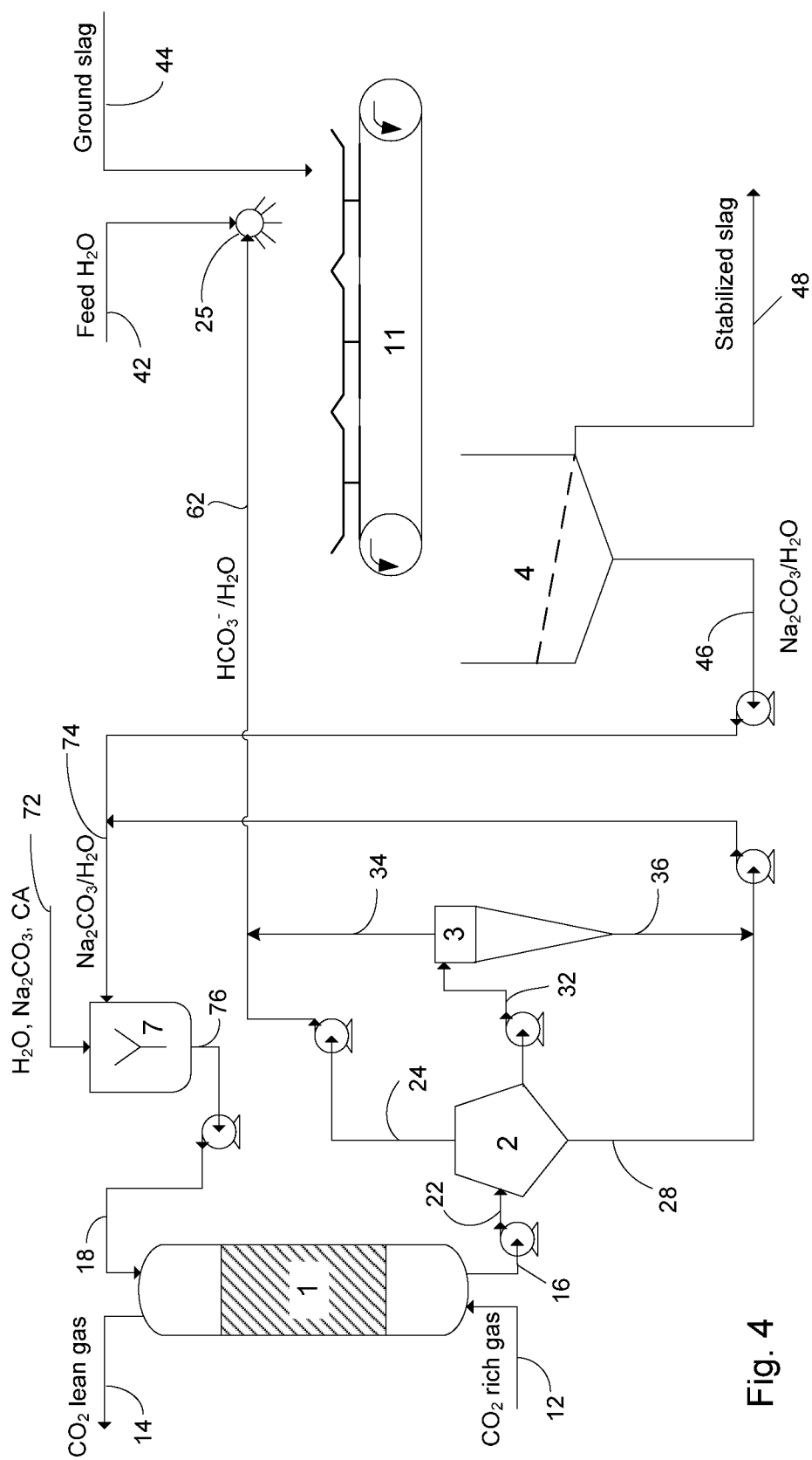


Fig. 4

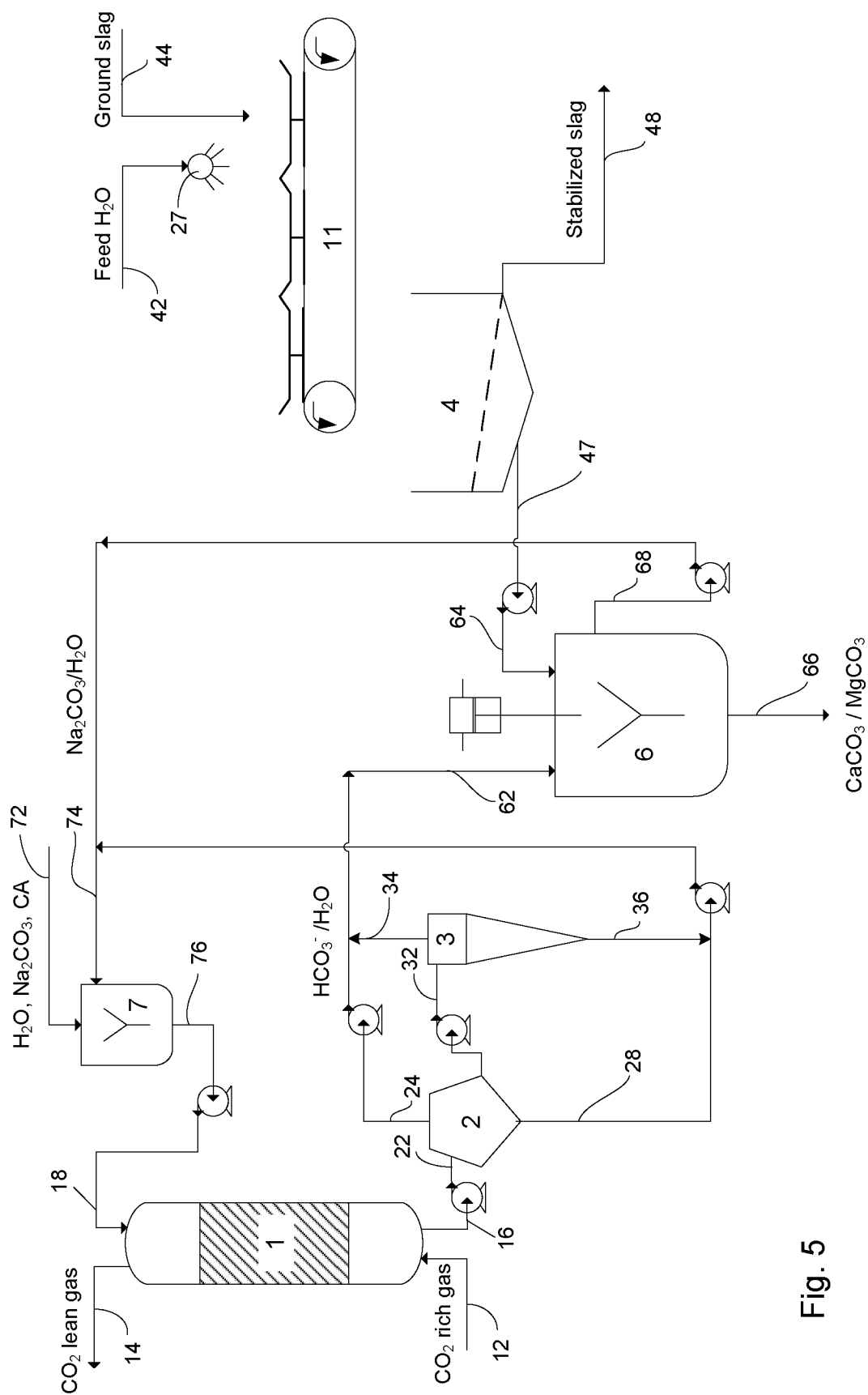


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2013/050514

A. CLASSIFICATION OF SUBJECT MATTER IPC: C21B 5/04 (2006.01) , B01D 53/62 (2006.01) , C12P 3/00 (2006.01) , C21B 3/04 (2006.01) , C22B 7/04 (2006.01) , C12N 9/88 (2006.01) 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) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) TotalPatent, STNEasy, Intellect (CPD) Keywords: slag, carbon dioxide, sodium carbonate, sodium bicarbonate, (calcium or magnesium)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 2,778,508 (GARTNER, E. et al.) 30 June 2011 (30-06-2011)	1, 2, 5, 6, 9-16 & 19-27
Y	Abstract; page 1, line 20 to page 3, line 17; page 4, lines 13-17 & 27-28; page 5, lines 1-21; page 6, lines 16-29; page 8, lines 11-17; page 9, lines 3-11; page 10, lines 3-32; page 11, line 1 to page 12, line 22; and claims 1-10.	3, 4, 7, 8, 17, 18
Y	WO 2007/071633 A1 (GEERLINGS, J.J.C. et al.) 28 June 2007 (28-06-2007)	3, 7, 8, 17 & 18
	Abstract; page 2, line 11 to page 3, line 7; page 3, line 18 to page 4, line 4; page 8, lines 15-28; and claims 1-7.	
Y	US 2009/0202410 A1 (KAWATRA, S.K. et al.) 13 August 2009 (13-08-2009)	4
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A	US 2012/0145047 A1 (CONSTANTZ, B.R. et al.) 14 June 2012 (14-06-2012)	
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A	CA 2,613,096 (BLAKE, S.W.M. et al.) 11 January 2007 (11-01-2007)	
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
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Date of the actual completion of the international search 15 August 2013 (15-08-2013)	Date of mailing of the international search report 19 September 2013 (19-09-2013)	
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Authorized officer Benjamin Chan (819) 934-3593	

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2013/050514

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