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UTILITY PATENT APPLICATION

**METHOD FOR SEQUESTERING CO₂ AND
SO₂ UTILIZING A PLURALITY OF WASTE STREAMS**

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METHOD FOR SEQUESTERING CO₂ AND SO₂ UTILIZING A PLURALITY OF WASTE STREAMS

PRIORITY

This application claims priority from provisional application 60/894,467 filed March 13, 2007

CONTRACTUAL ORIGIN OF THE INVENTION

The United States Government has rights in this invention pursuant to an employer/employee relationship between the U.S. Department of Energy (DOE) and the inventor, Yee Soong.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method for utilizing three waste streams to sequester flue gas constituent, and more particularly the present invention relates to a method for sequestering carbon dioxide and sulfur dioxide contained in flue gas by contacting the emissions with waste water brine pretreated with bauxite residue.

2. Background of the Invention

Many researchers suspect a link between global climate change and atmospheric concentrations of carbon dioxide (CO₂). Studies have shown a correlation between a rise in atmospheric CO₂ and increasing mean global temperature since the advent of the industrial era. In order to decrease the impact of CO₂ on global climate, several strategies are under development that will potentially remove CO₂ from the atmosphere or decrease CO₂ emissions.

Principle modes for carbon management include: (i) increasing the efficiency of energy conversion; (ii) using low-carbon or carbon-free energy sources; and (iii) capturing and sequestering anthropogenic CO₂ emissions. The latter strategy termed "CO₂ sequestration" permits continued use of fossil fuels for the generation of electric power while ensuring CO₂ emission reductions, and has gained increased attention in recent years. Various CO₂ sequestration options include oceanic-, terrestrial-, and geologic-

containment, and the use of advanced biological- and chemical-approaches. Each of these options has significant technical and economic hurdles that need to be addressed before being considered for full-scale application.

5 Geologic sequestration involves the capture of CO₂ from large point sources (such as fossil fuel-fired power plants) and the long-term storage of CO₂ in underground, brine-bearing geologic formations. Brine is an attractive reactant in CO₂ sequestration schemes inasmuch as 20-30 billion barrels of saline wastewater are produced annually in the United States as a byproduct of enhanced oil and gas recovery. About 65% of this water is reinjected into reservoirs for pressure maintenance, and the remaining water is treated and
10 discharged into surface water. In Pennsylvania, for example, a typical treatment cost for this wastewater can be as high as \$ 3.00/barrel. However, the pH of subsurface aquifer brines is typically low (approximately 3-5). The primary issue affecting solubility trapping is the limited absorptive capacity of brine. This low pH precludes dissolution of CO₂ and prevents carbonate formation.

15 Over 70 million tons of bauxite residue are generated annually when aluminum is extracted from the principal ore called bauxite (Aluminum Association, 2000). The residue is primarily comprised of iron and titanium oxides, silica, calcium carbonate, and unrecoverable alumina and caustic soda (NaOH), and, as such, is highly alkaline. The pH of the liquid reaches values as high as 13.5 (the hazardous threshold is 12.5) and the
20 solids and solid surfaces also contain high alkalinity. The caustic nature of the byproduct yields concerns of long-term environmental liability and impact because leakage of this alkaline liquid from impoundments into groundwater aquifers can result in mobility of several constituents of concern, including iron, aluminum, and hydroxide ion.

25 Worldwide, there are about 200 million tons of bauxite residues, the vast majority of which is stored in tailings ponds. Numerous methods have been attempted to mitigate the potential environmental impacts of the residue, including washing with seawater (Ward and Summers, 1993; Menzies et al., 2004), land application as a soil amendment (Lombi et al., 2002; Hughes, 2003), beneficial use as an admixture in cementitious materials (Singh et al., 1997; Zhihua et al., 2003), treatment of acidic mine drainage (Doye and
30 Duchesne, 2003), and sewage effluent treatment (López et al., 1998). However, large-

volume, economically-viable applications for dealing with bauxite residue have, as yet, not been identified.

The primary source of alkalinity in bauxite residue is NaOH remaining from the Bayer extraction of alumina. Other, more resilient, sources of alkalinity also impact the effectiveness of bauxite residue carbonation. Nikraz (2007) reported in *Journal of Materials in Civil Engineering* 19, Issue 1, pp. 2-9 that the effectiveness of carbonization treatment of the byproduct slurry is a function of the level of solid alkalinity present in the slurry as tri-calcium aluminate (TCA-6). However, TCA-6 is slow to react to be of any value as a sequestration reagent.

In geological sequestration, alkalinity buffering can be accomplished through mineral reaction within the host rocks, as noted by one of the inventors in Allen et al , *Fuel Process Tech.* 86, pp 1569-1580 (2005). However, due to sluggish reaction rates, these mineral reactions are likely to take a long time.

A need exists in the art for above-ground carbon sequestration methods of CO₂ and/or SO₂ by utilizing secondary production streams such as caustic bauxite tailings and acidic brine liquors. The methods should result in the treatment of the oxides as limiting reagents, with a concomitant decrease in volume and decrease in toxicity of all waste streams involved.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for sequestering carbon dioxide and/or sulfur dioxide that overcomes many of the disadvantages of the prior art.

Another object of the present invention is to provide a method for simultaneously reducing three unrelated waste streams. A feature of the invention is utilizing flue gas containing CO₂ and/or SO₂, utilizing bauxite, and utilizing brine wastewater. An advantage of the invention is that all three waste streams are minimized for long term sequestration

Yet another object of the present invention is to neutralize bauxite residue by utilizing two other and unrelated waste streams. A feature of the invention is reacting the bauxite with oil field brine and carbon dioxide. An advantage of the invention is decreasing the potential impact of the caustic residue by lowering its pH to at least 7.

Still another object of the present invention is to decrease saline wastewater volumes. A feature of the invention is utilizing the low pH wastewater to decrease the pH of bauxite residue, while simultaneously sequestering CO₂ and or SO₂ contained in flue effluent. An advantage of the invention is that saline wastewater produced from oil or gas well operations are reduced, both from an acidity standpoint and a volume standpoint.

Another object of the present invention is using bauxite residue and oil field brine mixtures to sequester acid gases such as carbon dioxide and sulfur dioxide. A feature of this invention is utilizing the bauxite residue as a caustic source while utilizing brine both as a source of calcium and magnesium ions to promote mineral carbonation and as a means of decreasing mixture viscosity to facilitate mass transfer and gas/slurry interaction. An advantage of the invention is a decrease in volumes of secondary waste streams generated by aluminum processing, oil/gas production, and combustion.

Still another object of the present invention is to provide an integrated process for utilizing a plurality of waste stream moieties as three reacting reagents in reducing the volume and environmental impact of the moieties. A feature of the invention is the capture and sequestration of both CO₂ and SO₂ from industrial gas byproduct streams, along with the concomitant treatment of bauxite residue and waste water brine. The advantages of this invention is the coincidental treatment of multiple industrial waste byproduct streams with little or no pretreatment of the streams necessary, thereby resulting in a low cost solution to dealing with the waste stream moieties.

The invention provides a method for sequestering CO₂ and or SO₂, the method comprising: using caustic bauxite tailings to increase the pH of brine fluid to above 7; and contacting the brine fluid with a second fluid containing acid gases for a time and at a temperature sufficient to mineralize the acid gases.

Also provided is a method to neutralize bauxite residue, the method comprising mixing the residue with waste water brine for a time and of a temperature sufficient to create a homogenous liquor; and contracting the liquor with a fluid containing combustion effluent for a time and at a temperature sufficient to decrease the pH of the residue by 40 percent.

DESCRIPTION OF THE DRAWING

Embodiments together with the above and other objects and advantages may best be understood from the following detailed description of the embodiment illustrated in the drawing, wherein:

5 FIG. 1 is a schematic diagram of the invented method, in accordance with features of the present invention;

FIG. 2 is a schematic diagram of a system for utilizing three waste streams to sequester greenhouse gases, in accordance with features of the present invention;

10 FIG. 3 is a graph showing percentages of reactants over time and their related pH values, in accordance with features of the present invention;

FIG. 4 is a table of the results of the CO₂ and SO₂ sequestration method conducted at 20 °C and 140 °C, in accordance with features of the present invention; and

FIG. 5 is a table of the experimental parameters associated with the CO₂ and SO₂ sequestration method, in accordance with features of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

15 The invented process contemporaneously removes both CO₂ and SO₂ from effluent fluids. This represents a significant improvement in sequestration strategy because separation of CO₂ and SO₂ from bulk gaseous byproduct stream is not necessary prior to treatment. The invented, integrated use of bauxite residue/brine mixtures in the process
20 provides a cost effective means of direct flue gas treatment and could be an attractive alternative for power plants located near bauxite residue tailings disposal sites. There is great interest from the aluminum industry to combine neutralization processes with CO₂ and SO₂ sequestration.

Specifically, the inventors found that mixtures of oil/gas wastewater brine and
25 bauxite residue can effectively sequester acid gases, including, but not limited to, CO₂, SO₂, NO, H₂S, and HCl, through a combination of solubility and long-term mineral trapping. The invented bauxite residue/brine mixture has a high alkalinity that can be used for neutralizing acid gases as well as acid waste materials. In such scenarios, the bauxite residue/brine mixtures were lowered to pHs of between 12.5 and 8.6, or lower. Surprisingly
30 and unexpectedly, the inventors found that mixing of bauxite residue and brine alone would

not be effective to neutralize bauxite residue. Rather, the reactions with CO₂, SO₂ and/or combinations thereof, are necessary to achieve complete neutralization (i.e., reducing the residue's pH to 6-7) of the bauxite residue. Carbonization product pH drifts to approximately 10.6 (From an initial 12.5 to 13.5 pH) as a result of excess CO₂ carbonation in the absence of brine. The proposed treatment method neutralizes the bauxite residue reactant, reducing the potential impact of the caustic byproducts to the surrounding environment.

The inventors have found that conversion of gaseous CO₂ into stable carbonate minerals is largely a function of pH, with observed increase in sequestration capacity observed at higher initial fluid pH, as disclosed in Soong et al., *Energy Conversion and Management* 45, pp. 1845-59 (2004), and incorporated herein by reference.

The inventors found that the bauxite residue/brine mixtures are just as effective in sequestering SO₂ that is present in industrial flue gases. Thus, the process removes both CO₂ and SO₂ from the gas stream contemporaneously.

As a secondary benefit, the described brine/CO₂ neutralization of bauxite residue generates a much lower volume of brine wastewater than do previously proposed methods of mixing of seawater with bauxite residue. In addition, the use of produced saline wastewater from oil or gas wells means that there is no net increase in saline wastewater generated.

The invented process can be conducted at a myriad of conditions. Typical conditions include ambient pressure and temperature. Pressures from ambient to 900 psig are suitable. Temperatures from 20 °C to 140 °C are suitable. Typical duration of the process can range from 0.5 hours to 5.5 hours.

A simplified schematic of the treatment process is designated as numeral 10 in Figure 1. A supply of bauxite residue 12 is procured from a myriad of secondary waste streams discussed supra (including, but not limited to aluminum processing centers, waste alkaline material sources generally, and fly ash producers such as large scale combustion and electricity generation facilities. No pretreatment such as sizing, grinding, solubilization or homogenizing of the bauxite residue is required. In its native state, the bauxite has a pH of between 13 and 13.5.

Wastewater brine 14 is mixed with the bauxite 12 to create a bauxite/brine mixture 16. Generally, the brine 14, which is also supplied in its untreated condition, has a pH of between 2.7 and 5

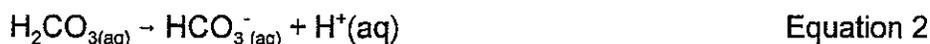
Mixture occurs at ambient temperatures. Beginning process temperatures between 20 °C and 40 °C are suitable. Process temperatures are likely to change due to the exothermicity of the process. Mixing of the bauxite and brine occurs until an homogenous liquor is produced, whereby the liquor exhibits a pH of between 8.5 and 12.5, and most preferably 10.5.

After the liquor equilibrates, a waste effluent fluid 18, such as flue gas, containing carbon dioxide, sulfur dioxide or both is contacted with the liquor. A myriad of mixing protocols are suitable. In one such protocol, all of the reactants are splash blended via mixing speeds between 500 revolutions per minute (rpm) and 1500 rpms. Typical reactions times are 30 minutes. The liquor is allowed to continue to react for an additional 30 minutes to assure complete reaction.

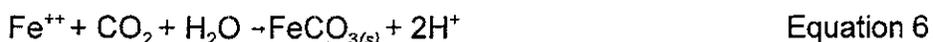
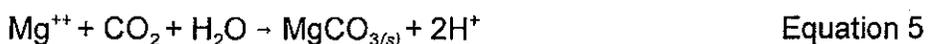
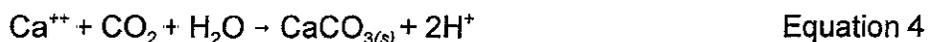
Bubbling of the flue gas (oxides) through the bauxite/brine mixture under continuous conditions is another suitable method for combining the reactants. Continuous conditions comprise providing a continuous flow of flue gas through the bauxite residue/brine mixture at a temperature (e.g. ambient) and pressure (e.g. 10 psig) sufficient to facilitate gas flow through the reactor. In this instance, typical reaction times are between 1 and 2 hours for a 90/10 bauxite residue/brine mix and 70/30 bauxite residue/brine mix, respectively. Generally, contact of the fluid to the liquor continues for a time and at a pressure and temperature sufficient to cause the oxides to convert to carbonates 20, per Equations 4-6, infra. Generally, ambient temperature and pressures are suitable. However, flue gas temperatures of as high as 60 °C will suffice. This allows for the process to be utilized with minimal pretreatment of flue gas effluent.

Treated flue gas effluent 22 is then either vented to the atmosphere, recycled or else processed in another scrubbing method.

Dissolution of CO_2 in water results in the formation of carbonic acid (H_2CO_3) that dissociates to HCO_3^- and CO_3^{2-} ions, releasing H^+ to the fluid:



Therefore, dissolution of CO_2 results in a decrease in pH. A decrease in pH is further enhanced when carbonate minerals precipitate from ions in solution via reactions such as:



Thus, carbonate precipitation in the absence of buffered pH is limited by the generation of H^+ which acts to consume alkalinity, ultimately resulting in increased solubility of calcite and other carbonate minerals.

Some brines have a high concentration of Ca, Mg and Fe in addition to the dominant Na and Cl ions. Under favorable conditions (pH, temperature, pressure), the Ca, Mg and Fe from brine could react with CO_2 to ultimately produce CaCO_3 (s), MgCO_3 (s), Fe_2CO_3 (s) and other mineral products that would safely and permanently store CO_2 . As dictated by the carbonate system disclosed herein, a solution pH of 7.8 or higher achieves substantial dissolution of CO_2 and subsequent mineral carbonate formation. Therefore, to favor CO_2 dissolution and precipitation of mineral carbonates, the inventors have increased the pH of wastewater brine to make it a more viable reactant with greenhouse gas effluent. This fixes the pH at relatively high values in order to counteract the loss of alkalinity (production of H^+) during mineral precipitation and CO_2 dissolution.

CO₂ and Flue Gas CO₂ Treatment Protocol Detail

The invented process treats the acid gas moiety as the limiting reagent, as such, as long as target pH values are attained, and the suitable cations are present in adequate concentrations, any concentration of CO_2 , SO_2 , and other acid gases can be carbonized and otherwise sequestered. For illustrative purposes only, data presented herein deal with CO_2 and SO_2 , but the application of the invented process should not be relegated to these two species. Experiments were conducted in the laboratory via a bench top processor, so

designated as numeral 30 in FIG. 2 whereby 15 percent by volume of the flue gas was CO₂. However, neat CO₂ streams, (i.e., 100 percent by volume CO₂, or substantially 100 percent by volume CO₂) are also treatable with the invented protocol.

5 The experiments confirmed the efficiency of the invention to sequester CO₂ in bauxite residue/brine mixtures at a series of temperatures, CO₂ pressures, and brine/bauxite residue mixture ratios. Those ratios are depicted in FIG. 3. FIG. 3 shows the pH of bauxite residue/brine mixtures and CO₂ carbonated product in 10 percent increments by volume.

10 The experiment was conducted at room temperature with an initial CO₂ head space pressure of 100 psig, which translates into a 666 psig head space pressure of flue gas inasmuch as CO₂ comprises 15 volume percent of typical flue gas effluent. Suitable ratios of CO₂ to the bauxite residue-brine liquor are selected between 2 kg CO₂/kiloliter of liquor and 9kg CO₂/kiloliter of liquor. Preferable ratios are between 3.5 and 7.9. Preferable ratios are selected empirically, depending on the sequestering conditions such as temperature and the bauxite residue/brine ratio. Pure CO₂ feed experiments and flue gas experiments indicate that the invented process can treat flue gas directly without costly separation of CO₂ from the effluent stream.

15 Bauxite residue/brine mixture carbonation experiments were carried out in a half-liter autoclave (Hastelloy C-276) manufactured by Progressive Equipment Corp., (element 32 in FIG. 2) and a similar one-liter autoclave reactor. The reactor 32 was loaded with 180 ml of premixed reactant (brine and bauxite residue mixture 34) and the head space 36 of the reactor was purged with 15 psig carbon dioxide three times to remove all room air from the head space. A prescribed initial pressure of CO₂ (element 38 in FIG. 2), typically 100 psig, was charged into the reactor to achieve the desired initial pressure. Valves were closed and the bauxite residue/brine-CO₂ mixture was agitated at a selected speed to prevent settling of precipitate during the experiments and promote CO₂ dissolution. Upon completion of each experiment, the slurry was cooled to room temperature, the remaining head space pressure noted, and the remainder vented. The slurry was removed from the reactor and filtered to separate the solids from the aqueous solution. A digital pH meter (Sentron-1001 pH) was used to determine the pH of the solution before and after reaction.

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A series of reactions (100 psig initial pressure, room temperature) were carried out across the full range of bauxite residue/brine mixtures in 10% by volume increments

Carbonation experiments were carried out for approximately two hours after pressure stabilization was observed. Head space pressure stabilization was assumed to indicate that the reactor contents had achieved short-term equilibrium. In experiments using pure CO₂, the pressure change between the initial application and final equilibrium condition was used with initial and final system temperature to estimate the short-term capacity of the bauxite residue/brine mixture to sequester CO₂, assuming ideal behavior of gas under the applied conditions.

The inventors found that the capacity of reactant mixtures to absorb CO₂ is primarily a function of reactant mixture pH. Carbonation capacity decreases at lower pH (i.e., with decreasing mixture bauxite residue concentration and increasing mixture brine concentration). The rate of CO₂ dissolution in the reactive mixture was observed to decrease with increasing bauxite residue composition (increasing brine), when mixed at 500 RPM as was done for all batch experiment described herein. This illustrates that the increasing mixture viscosity with increasing bauxite residue composition requires an increased total energy input to achieve complete CO₂ gas reaction. Thus, the inventors have further discovered the benefit of mixing brine with bauxite residue to minimize viscosity and therefore facilitate slurry reaction and conveyance.

Pure CO₂ carbonation of brine/bauxite residue in mixtures with as little as 20% brine can be fully and permanently neutralized. In contrast, neutralization of bauxite residue with brine only (i.e., without CO₂ and SO₂ addition) can require mixtures with brine composition greater than 95%, as described earlier. Comparison with the currently employed technique of batch carbonation of pure bauxite residue slurry using pure CO₂ shows the advantages of the invented treatment method. In the currently employed method, bauxite residue pH initially dropped from 13 to between 8 and 8.5 by direct carbonation. However, following treatment, the pH rises back to between 10 and 11 as a combined result of partial decarbonation and slower reaction with solid-phase alkalinity. Results shown in Figure 3 show that, while initial bauxite residue/brine mixtures do not achieve neutralization,

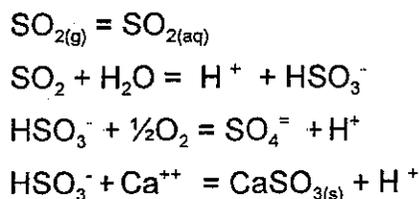
carbonation of bauxite residue/brine mixtures regularly results in complete product neutralization for most of the carbonation reactions.

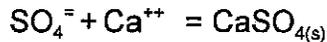
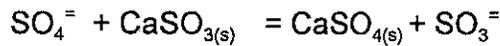
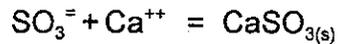
Analyses of reactant and product ionic concentrations provided insight into the initial leachability of constituents of concern, and the potential environmental impact of the treated product on the environment as compared to the individual reactants and the bauxite residue/brine mixture. In the short term, calcium, strontium, and sodium concentrations do not appear to change in reactant mixtures as a result of CO₂ carbonation. As illustrated in Figure 3, high percent bauxite residue reactant mixtures (up to 60%) have a relatively high pH (between 10.5 and 11). In this pH range, magnesium ion present as a result of brine addition rapidly precipitates as magnesium hydroxide. However, following reactant mixture carbonation, overall solution pH drops and magnesium hydroxide is redissolved.

SO₂ and Flue Gas SO₂ Treatment Protocol Detail

In addition to carbon sequestration efficacy of bauxite residue slurries, and the bauxite residue slurry neutralizing capacity of CO₂ from the industrial byproduct gas stream, caustic bauxite residue/brine mixtures are also effective in sequestering SO₂ that is present in industrial flue gases. The method is suitable to mineralize effluent wherein SO₂ is present at between 100 parts per million (ppm) and 1,000 ppm. Typical effluent concentrations of SO₂ are about 540 ppm.

Initially, SO₂ dissolves readily in water. Following dissolution, the SO_{2(aq)} dissociates and speciates according to the solution conditions and the sulfurous acid cycle. Reaction with calcium ions will result in calcium sulfite formation. Partial oxidation of sulfite or bisulfite to sulfate will also allow formation of calcium sulfate and precipitation of mineral gypsum. These reactions are summarized below.





5 Caustic bauxite residue serves as an effective caustic reagent to promote SO₂ absorption. This treatment removes both CO₂ and SO₂ from the gas stream simultaneously. This represents a significant improvement in sequestration strategy because separation of CO₂ and SO₂ is not necessary prior to bauxite residue/brine mixture carbonation.

10 Bauxite residue contains significant quantities of iron oxide, suggesting that similar reactions may occur. SO₂ in the gas mixture reduces Fe⁺⁺⁺ to Fe⁺⁺ which then results in the formation of FeCO₃ (siderite) and FeS₂ (pyrite). Moreover, Ca in the bauxite residue/brine mixture will allow formation of calcium sulfite/sulfate.

15 Flue gas experiments (3.73% O₂, 80.69% N₂, 15.53% CO₂, 542 ppm SO₂) were conducted in a 1 liter autoclave reactor with various brine/bauxite residue ratio at a constant stirring speed of 1,500 rpm at different temperatures (20 and 140 °C) and reaction time of 1 to 5 hrs. The results are described in FIGS. 4 and 5. These results demonstrate that SO₂ can be effectively absorbed

20 These results demonstrate that SO₂ can be effectively absorbed into bauxite residue/ brine at 20 °C (Run #405, 95.3% SO₂ removal), and yet more complete when mixed with bauxite residue slurries at higher temperature of 140 °C (Runs #408, and 409, 99.9% in both cases). The SO₂ sequestering capacity of bauxite residue slurry/brine mixtures is comparable to that of pure bauxite residue slurry (Run #407, 99.9%), but the volume of mixture available for treatment using such mixtures would be greater as a result of bauxite residue dilution in brine. This demonstrates that reacting mixtures of bauxite residue slurry and brine with SO₂-bearing industrial waste gasses is an improvement over
25 treatment of such gasses with pure bauxite residue or pure brine alone.

30 All runs except Run #410 were conducted with a simulated flue gas that contained both SO₂ and CO₂, and so all described SO₂ removal occurred coincidentally with CO₂ sequestration. CO₂ capture is greatest in mixtures of bauxite residue slurry and brine. In comparison, those reactions including bauxite residue liquid (no slurry solids) and brine

(Runs #405, 406) at 20 °C had roughly half the CO₂ bearing capacity of the bauxite residue slurry/brine mixtures that were directly reacted with simulated flue gas at 140 °C (Runs #408, 409). These bauxite residue slurry/brine mixtures had greater capacity than even that of the pure bauxite residue slurry (Run #407); evidence of a symbiotic interaction
5 between bauxite residue slurry/brine in the mixture. This data shows that mixtures of bauxite residue slurry and brine have demonstrated advantages over single component reaction for both the sequestration of CO₂ and SO₂ in mixed industrial byproduct gas streams.

10 Furthermore, the heretofore caustic and acid waste streams associated with bauxite residues (pH 12.5 to 13.5) and wastewater brine (pH 3 to 5) respectively, are effectively neutralized after participating as reactive reagents in the invented process such that the resulting brine/bauxite residue liquor has a pH of between 9 and 12 prior to reaction with acid gas moieties and a pH of between 5.5 and 7.5 after reaction with acid gas moieties.

15 The final product, that is the fully neutralized bauxite residue/brine mixture treated with and containing sequestered, mineralized acid gas has a pH of between approximately 6 and 7.

20 While the invention has been described with reference to certain embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from its scope. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed, but that the invention will include all embodiments falling within the scope of the appended claims.