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Method for Producing Hydrogen Fuel, Zinc Powder, Zinc Oxide, Polymetallic Matte Bullion, and Potable Water from Zinc Ore

Provisional Patent Application of James H. Hawley III
on behalf of Blackstone Green Energy, Inc.

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for

TITLE: Method for Producing Hydrogen Fuel, Zinc Powder, Zinc Oxide, Polymetallic Matte Bullion, and Potable Water from Zinc Ore

CROSS-REFERENCE TO RELATED RESEARCH: None

FEDERALLY SPONSORED RESEARCH: None

SEQUENCE LISTING: None

BACKGROUND OF THE INVENTION

This invention relates to the processing of zinc-rich ores, specifically for purposes of creating hydrogen fuel, zinc oxide, zinc powder, polymetallic matte bullion, and potable water. The invention arose from the inventor's 40 years of experience in developing the Blackstone Mine ("Blackstone") in Elmore County, Idaho, approximately 80 miles southeast of Boise.

The Blackstone ore body is particularly rich in zinc. Depending on the level of refinement, zinc has a number of important industrial and pharmaceutical uses. In industry, zinc is most commonly used as an anti-corrosion agent in the galvanization of other metals (Green and Earnshaw, 1203). A widely used alloy that contains zinc is brass, in which copper is alloyed with anywhere from 3 percent to 45 percent zinc, depending upon the type of brass. (Lehto, 829). Besenhard notes that zinc is frequently employed as an anode material for batteries. Zinc oxide compounds are often used as a white pigment in paints and as a catalyst in the manufacturing of rubber (Emsley, 503).

Zinc is also considered to be an essential mineral for the maintenance of public health (Hambidge and Krebs, 1101–5). It is included in most single tablet over-the-counter daily vitamin and mineral supplements (DiSilvestro, 135, 155). Pharmaceutical preparations include zinc oxide, zinc acetate, and zinc gluconate. Zinc is believed to possess antioxidant properties, which may protect against accelerated aging of the skin and muscles of the body. It helps speed up the healing process after an injury (Milbury and Richer, 99) and is suspected of being beneficial to the body's immune system (Keen and Gershwin, 415–31). Zinc deficiency has been linked to major depressive disorders (Swardfager et al., 911-29).

Although zinc is the 24th most abundant element in the earth's crust, recent research suggests that known zinc reserves – at least those that can be mined profitably at current prices – may soon be exhausted, particularly given the recent closure of several major zinc mines (Shumsky, par. 1; Troen, par. 10). Zinc output lagged consumption by 296,000 tons in 2014, according to the International Lead and Zinc Study Group (de Sousa and Clarke, par. 7). This research suggests that either new zinc reserves must be discovered or the price of zinc must increase significantly to offset the cost of mining currently known, but less accessible, reserves.

PRIOR ART

The technology for recovering zinc from waste and recycled materials has been known since at least 1888. For example, the Waelz process is a method of recovering zinc and other relatively low boiling point metals from EAF flue dust and other materials using a rotary kiln (Harris, 702-720). The process consists of treating zinc-containing material (in which zinc can be in the form of zinc oxide, zinc silicate, zinc ferrite, or zinc sulphide) together with a carbon-containing reductant/fuel within a rotary kiln at 1000° C to 1500° C. The kiln feed containing zinc "waste," along with the fluxes and reductant (coke), are typically pelletized before being added to the kiln. The chemical process involves the reduction of zinc compounds to elemental zinc (boiling point 907° C) which volatilizes, oxidizing in the vapor phase to zinc oxide. The zinc oxide is collected from the kiln outlet exhaust by filters or electrostatic precipitators and settling chambers.

In the indirect process, metallic zinc is melted in a graphite crucible and vaporized at temperatures above 907° C. Zinc vapor reacts with the oxygen in the air to produce zinc oxide, accompanied by a drop in its temperature and bright luminescence. Zinc oxide particles are transported into a cooling duct and collected in a baghouse. This method was popularized in 1844 by French painter E.C. LeClaire and is commonly known as the French process (Holley, 153). Its product normally consists of agglomerated zinc oxide particles with an average size of 0.1 to a few micrometers. Measured by weight, most of the world's zinc oxide is manufactured via the French process.

More recently, University of Delaware researchers tested a solar reactor they developed to produce hydrogen from sunlight (Roberts, par. 1). Eight weeks of sophisticated testing at temperatures up to 1200° C revealed that the reactor's mechanical, electrical, and thermal systems worked as predicted. The researchers were even able to collect small amounts of the stored solar energy in a vial, despite operating below critical reaction temperatures. The reactor is designed to accommodate a two-step water-splitting process to generate hydrogen renewably from sunlight. The reactor, which is closed to the atmosphere, uses gravity to feed zinc oxide powder (the reactant) into the system through hoppers that dispense the powder onto a ceramic surface. There it undergoes a thermochemical reaction upon exposure to highly concentrated sunlight within the reaction cavity, producing solar fuel.

A research team from the University of Colorado incorporated desalination into microbial fuel cells, a new technology that can treat wastewater and produce electricity simultaneously (Luo, Jenkins, and Wren, 340-344). They were able produce hydrogen gas, which is collectable and storable, thus making improvements in the technology, although the practicality of their process remains in question.

Stanford University scientists have created an advanced zinc-air battery with higher catalytic activity and durability than similar batteries made with platinum and other costly catalysts (Li, 1805; Shwartz, par. 1). The researchers believe their discovery could lead to the development of a low-cost alternative to conventional lithium-ion technology.

Two pyrometallurgical processes have been designed and developed for the treatment of zinc-containing wastes:

1. High-temperature submerged plasma zinc fuming process; and
2. Reductive roast followed by oxidative ISASMELT process (Versheure, 237-251).

Continuous operation of these processes has been demonstrated on a pilot scale. It has been shown that high zinc-fuming rates can be obtained while retaining vessel integrity through the formation of a stable freeze lining. A mathematical process model using FactSage and ChemApp thermodynamic software has been developed, which simultaneously describes chemical, thermal, and heat transfer outcomes of these processes.

The chemistry of producing hydrogen through the dissociation of zinc oxide is also well known. In 2005, a team of scientists at the Weitzman Institute in Israel introduced an energy self-sufficient hydrogen-production process by dissociating zinc oxide with a solar reactor to produce zinc powder (Piquepaille, par. 8). The powder was mixed with 350˚ C water to produce hydrogen, reprecipitate the zinc oxide for further dissociation, and then reused to produce more hydrogen. Promising as this research was, the project did not address the production of the zinc oxide catalyst used to make the zinc powder, nor did it address the energy required to create the compound.

In contrast, the invention begins at the source through the vaporization of zinc ore. The invention is an end-to-end process designed for the production of hydrogen fuel, zinc oxide, zinc powder, matte bullion (copper, silver, lead, and gold), and potable water from ore containing sufficient amounts of zinc to allow self-sustaining hydrogen production. Ore containing 3 percent zinc (60 lbs/ton) is sufficient for the invention to generate a self-sustaining hydrolysis reaction.

Hydrogen fuel produced from the reaction is used to power a high-temperature reactor for dissociating zinc oxide into zinc powder, which can then be used to make additional hydrogen by repeating the hydrolysis reaction multiple times from the initial charge of zinc ore. Zinc powder is easier to handle and can be safely transported to power plants and fuel depots where hydrogen fuel could be easily generated on-site using zinc hydrolysis. Instead of coal- or gas-fired power plants, zinc powder can be a far more efficient, inexpensive, and environmentally friendly energy source.

Insofar as I am aware, there is no truly self-powered processing circuit for the production of zinc powder directly from zinc ore. I believe the invention overcomes this obstacle by creating a sustainable hydrogen-production process that requires no fuel sources beyond the hydrogen produced from the ore itself. With fewer than 40 hydrogen fuel stations in the United States, the widespread use of hydrogen-powered vehicles has been stunted. Zinc powder offers a viable method for hydrogen production at the point-of-use, ultimately clearing the way for widespread distribution of hydrogen fuel and an excellent alternative to burning fossil fuel. In the not-too-distant future, drums of zinc powder could become the replacement for barrels of oil.

SUMMARY

The invention seeks to replace the use of fossil fuels expended in previous production methods of hydrogen gas; instead, relying on water electrolysis and thermochemical reactions using metallic oxides and powders. Conventional electrolytic production of hydrogen requires 4.5 times more energy than is produced from the hydrogen generated, making the process self-defeating as an energy-neutral method. The advantages to the invention include, but are not necessarily limited to:

1. Economical hydrogen production
2. Energy self-sufficiency
3. Zero environmental emissions
4. Clean energy
5. Fewer greenhouse gasses
6. Reduced carbon footprint
7. On-site portable hydrogen production
8. Wider hydrogen distribution channel
9. Advancing the use of electrical vehicles
10. Viable alternative to fossil fuels
11. Alternative fuel for electrical generation
12. Alternative power for desalination
13. Potable water production
14. Solar power storage

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts the entire self-sustaining ore processing circuit for creating hydrogen fuel, zinc oxide, zinc powder, and a polymetallic matte consisting of copper, silver, and gold. Figure 2 details the crushing, grinding, and screening circuit more broadly referenced in Figure 1.

DETAILED DESCRIPTION AND OPERATION

An ore-processing circuit is provided in which raw ore (1.1) Finely ground zinc ore (-200 mesh) is roasted at a temperature at or above 400° C in a closed-circuit rotary kiln to remove the sulfur content of the ore feed.(1.5). Three-phase electrical current for the kiln is provided by a hydrogen-powered internal combustion engine (ICE) coupled to an electrical generator operating at 3600 rpm (1.4). A 35 Kw solar panel array and electrical converter act as a backup power supply for the kiln in the event power from the ICE generator is unavailable.

The dry ground roasted ore is conveyed to an electric kiln (1.5). After the ore is fired at a temperature of about 1000° C for approximately two to three hours, the zinc content in the ore vaporizes and the vapor stream vents to a hydrolysis reactor and zinc oxide filtering vessel (1.8) where water (1.6) is introduced into the vapor stream to strip the H2 molecule from the water, producing hydrogen gas and precipitating zinc oxide from the vapor stream (1.9). Firing continues at 1200° C to 1300° C, where metallic copper, silver, and gold collect at the base of the kiln, the impurities collect in a borax glass slag layer floating on top of the metals. The metals and slag are tapped from the base of the kiln into a matte bullion containing copper, silver, lead, and gold (1.11). The zinc oxide is pneumatically removed from the filter cartridges in the hydrolysis reactor to an automated packaging system for distribution to market or retained for production of zinc powder in a solar/hydrogen powered zinc oxide dissociation reactor (1.10) the polymetallic matte bullion produced in the second temperature phase is shipped to a refiner for final separation.

The entire processing circuit is self-sustaining insofar as hydrogen fuel is carried from the hydrogen reactor and zinc oxide filtering vessel (1.8) to a hydrogen-powered generator (1.4). Excess hydrogen fuel is sent to storage tanks (1.13) for later use in the processing circuit. Water from the hydrogen/zinc oxide reaction (1.12) can be reused in the hydrogen reactor (1.8) or used as potable water.

The entire zinc-to-hydrogen and zinc oxide processing circuit uses no fossil fuels, relying solely on the hydrogen produced during the processing cycle and solar energy.

Figure 2 details the crushing, grinding, roasting, and screening process broadly referenced in Figure 1 (1.2). Ore is analyzed for zinc content using handheld X-ray fluorescence (2.2). Ore containing at least 60 pounds per ton of zinc (3 percent) is sent to a jaw crusher (2.3) where it is crushed to -3/4-inch and conveyed to a pulverizer where it is ground to -200 mesh. A circular vibrating screen (2.4) removes oversized ore, and returns it (2.5) to the pulverizer for regrinding (2.6). Properly sized ore is then conveyed (2.7) to a rotary kiln for roasting and the electric kiln for the first-stage firing (1000° C) and zinc vaporization (also known as “zinc fuming”). The vapor stream vents to a hydrogen reactor and zinc oxide filtration system (commonly known as a baghouse) where the introduction of water liberates hydrogen gas by stripping the hydrogen molecule from the water. Zinc oxide precipitates as a non-toxic white powder as the zinc vapor stream cools.

Following the zinc/hydrogen/water reaction (2.8), borax glass and sodium carbonate (soda ash) are added to the residual ore (calcine) from an overhead mixer. With the addition of the reagents to the calcine, the kiln temperature is raised to between 1200° C to 1300° C (second-stage firing). Fluxes absorb the impurities into a liquid slag layer that forms on the top of the molten copper, silver, lead, and gold. The metals are poured into molds as a polymetallic matte and further refined into pure metals at a third-party refinery (2.14), while the borax slag is reused or recycled.

The invention is designed to create a self-perpetuating energy cycle for the production of hydrogen, zinc oxide, and zinc powder with near-zero atmospheric emissions. The invention uses no fossil fuel in its processing cycles. Standby solar energy and excess hydrogen from previous hydrolysis cycles are utilized only if the zinc content in the ore falls below the minimum 3 percent requirement needed for self-sufficient production of hydrogen fuel. With regard to standby solar energy, the invention includes a method for the storage of solar energy in zinc oxide coatings on the collector panels and zinc powder/silver storage batteries.

The invention includes proprietary designs for a graphite-lined electric kiln to tap molten metals from its base and boil off zinc into a vapor-transport system connected to a hydrolysis reactor. The kiln has two controlled heating phases. The first phase takes place at or near 1000° C for vaporizing the zinc content in the ore; the second phase occurs at 1200° C to 1300° C for reducing the remaining calcine into matte bullion (metal bars).

The invention includes the design of a hydrolysis reactor and zinc oxide pneumatic filtering system for producing hydrogen and zinc oxide from the zinc vapor stream during the hydrolysis reaction. The vessel and filters are designed to capture and then pneumatically release zinc oxide from filter cartridges as the zinc oxide powder precipitates from the zinc vapor stream upon reacting with water. Zinc oxide is pneumatically conveyed to storage containers, zinc oxide dissociation reactor, or an automated packaging machine depending on the intended use of the zinc oxide.

A portion of the hydrogen gas generated from the primary processing phase (zinc fuming) is used to operate electrical generators for powering the kilns, equipment and vehicles required to load, crush, screen, grind, and transport zinc ore into the invention's ore processing circuit.

The invention also includes a solar-powered rotary receiver/reactor for the solar thermal dissociation of zinc oxide, made of sintered zinc oxide tiles encasing a porous aluminum oxide and silicon dioxide insulation, reinforced by a ceramic composite lining designed to produce temperatures in excess of 1800° C for the production of zinc powder from zinc oxide. The reactor will accommodate biomass fuel or inert gas to lower the dissociation point of zinc oxide to elemental zinc from 1794° C to a projected low of 1300° C to 1500° C.

The invention's kiln, reactor, control valves, pumps, conveyors, reagent feeders, metering devices, and sensors are controlled by proprietary computer software authored by the inventor. The invention includes an additional design for a portable hydrogen gas-production circuit using the zinc powder manufactured by the hydrolysis reactor from the primary invention described above. The zinc powder is mixed with superheated sea, waste or tap water at 350° C to produce on-site hydrogen for point-of-use hydrogen dispensaries, industrial fueling depots, power plants, desalination plants, and any other facility either capable or can be modified to operate on hydrogen as a fuel.

While the zinc and superheated water process is a well-known prior-art chemical reaction for hydrogen gas production, the invention differentiates itself through its zinc fuming from zinc ore, zinc oxide dissociation, solar energy storage used in on-site production, and portability in the fossil fuel free production hydrogen (green hydrogen). The invention seeks to widen the distribution of hydrogen gas as a clean, environmentally friendly fuel for the reduction of fossil fuel use and hydrocarbon emissions.

The foregoing invention has been described in accordance with relevant legal standards, thus the description is exemplary rather than limiting in nature. Variations and modifications to the disclosed embodiment may become apparent to those skilled in the art and fall within the scope of the invention.

REFERENCE NUMERALS

Figure 1

1.1 Zinc ore
1.2 Crush and grind
1.3 Solar panel array
1.4 Rotary kiln (≥400° C) to remove sulfur
1.5 Hydrogen-powered generator
1.6 Electric kiln
1.7 Air/water injection
1.8 Hydrogen/zinc oxide filter vessel
1.9 Zinc vaporization process
1.10 Zinc oxide production
1.11 Packaging and marketing
1.12 Copper, silver, and gold matte production
1.13 Potable water production
1.14 Excess hydrogen fuel to storage

Figure 2

2.1 Zinc ore

2.2 Grading ore for zinc content

2.3 Crushing and grinding to ¼-inch gravel

2.4 Circulatory vibrating screen

2.5 Oversized return conveyor

2.6 Pulverization of ore to -200 mesh

2.7 Ore feed conveyor

2.8 Ore/reagent mixer

2.9 Kiln gantry hoist

2.10 Rotary kiln (≥400° C) to remove sulfur

2.11 Electric kiln

2.12 Zinc oxide recovery filter

2.13 Packaging and marketing

2.14 Pouring copper, silver, and gold ores into metallic matte

2.15 Shipment to third-party smelter for refining and certification

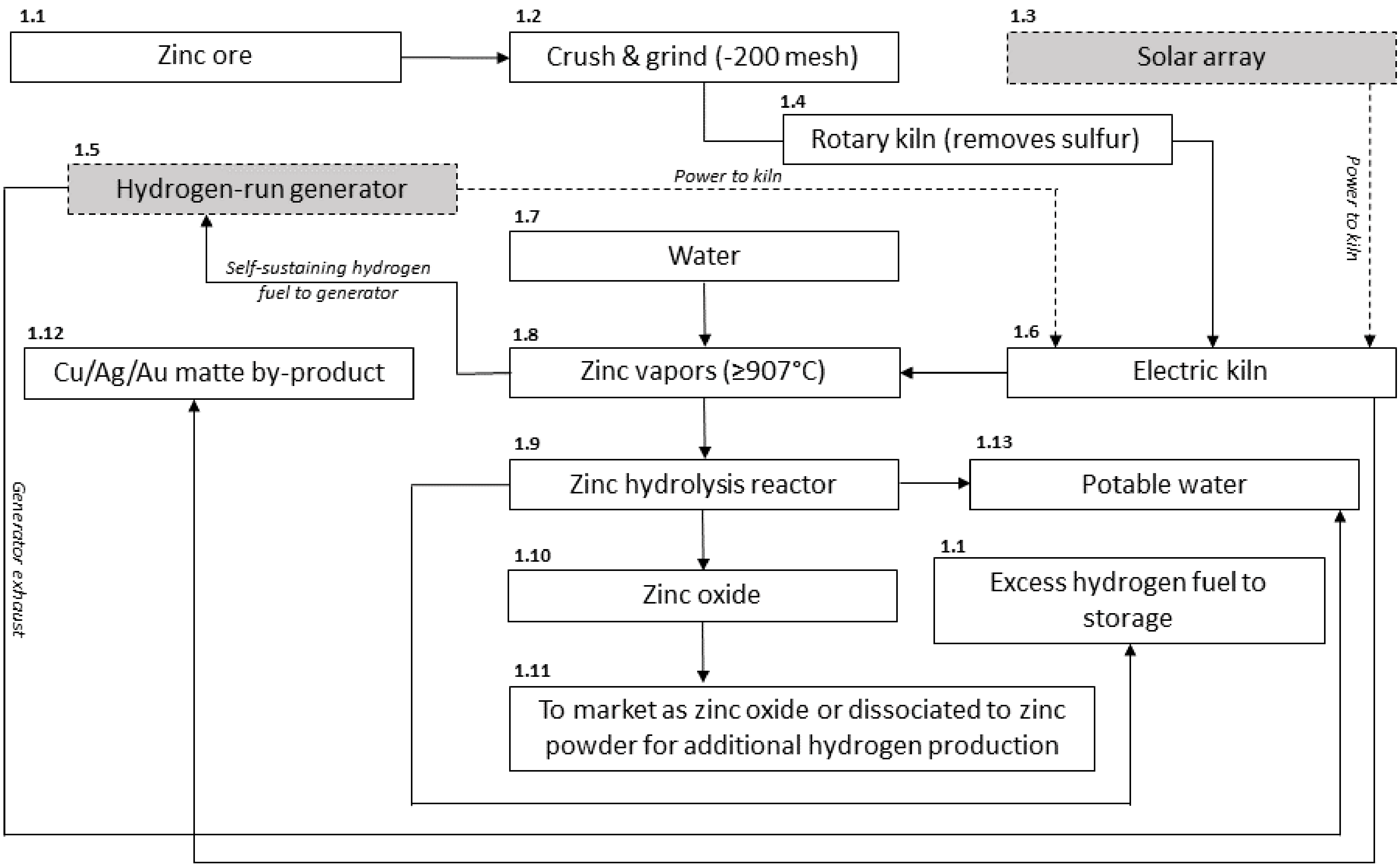
CLAIMS

What is claimed is:

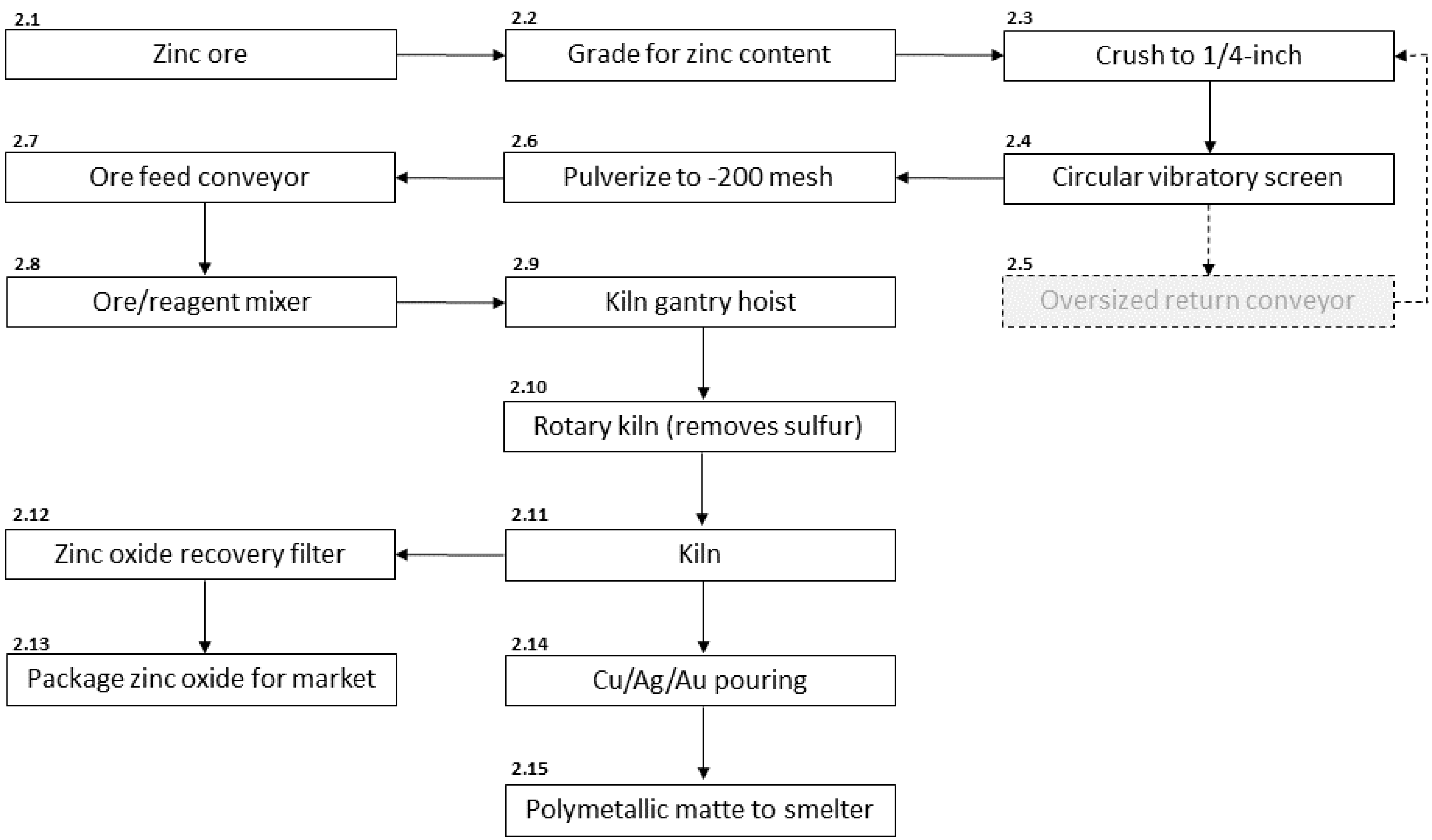
1. An environmentally safe, closed-circuit method for processing zinc ores into hydrogen fuel, zinc oxide, zinc powder, and potable water substantially as shown and described.

2. A technology utilizing zinc oxide and zinc powder for improving the efficiency in photo-voltaic cells and panels. The technology consists of absorption coatings for solar receptors and the storage of solar energy. Unlike the use of such coating in miniature photo-voltaic cells, as in experiments at the University of Arkansas, the claimant intends to expand the coating technologies to large-scale solar collectors that will simultaneously store solar energy for later use. The claimant intends to expand the invention into a highly efficient, large-scale photovoltaic cells capable of storing significant amounts of reserve energy when sunlight is unavailable.

Provisional patent application
of James H. Hawley III
Method for producing hydrogen fuel . . . from zinc ore
Figure 1 of 2



Provisional patent application
of James H. Hawley III
Method for producing hydrogen fuel . . . from zinc ore
Figure 2 of 2



ABSTRACT

An environmentally friendly closed circuit for processing zinc-rich ores into hydrogen fuel, zinc powder, zinc oxide, and potable water is described. The invention replaces the use of fossil fuels expended in current production methods of hydrogen gas; instead relying on water electrolysis and thermochemical reactions using metallic oxides and powders. Conventional electrolytic production of hydrogen requires 4.5 times more energy than is produced from the hydrogen generated; steam reformation requires three times as much energy. Both are self-defeating as energy-neutral methods. In the case of the steam reformation, each ton of hydrogen produced releases nine or more tons of carbon dioxide, carbon monoxide, and other noxious pollutants into the atmosphere, significantly contributing to climate change (Collodi and Wheeler, 37).

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