No. 669,410. Patented Mar. 5, 1901.

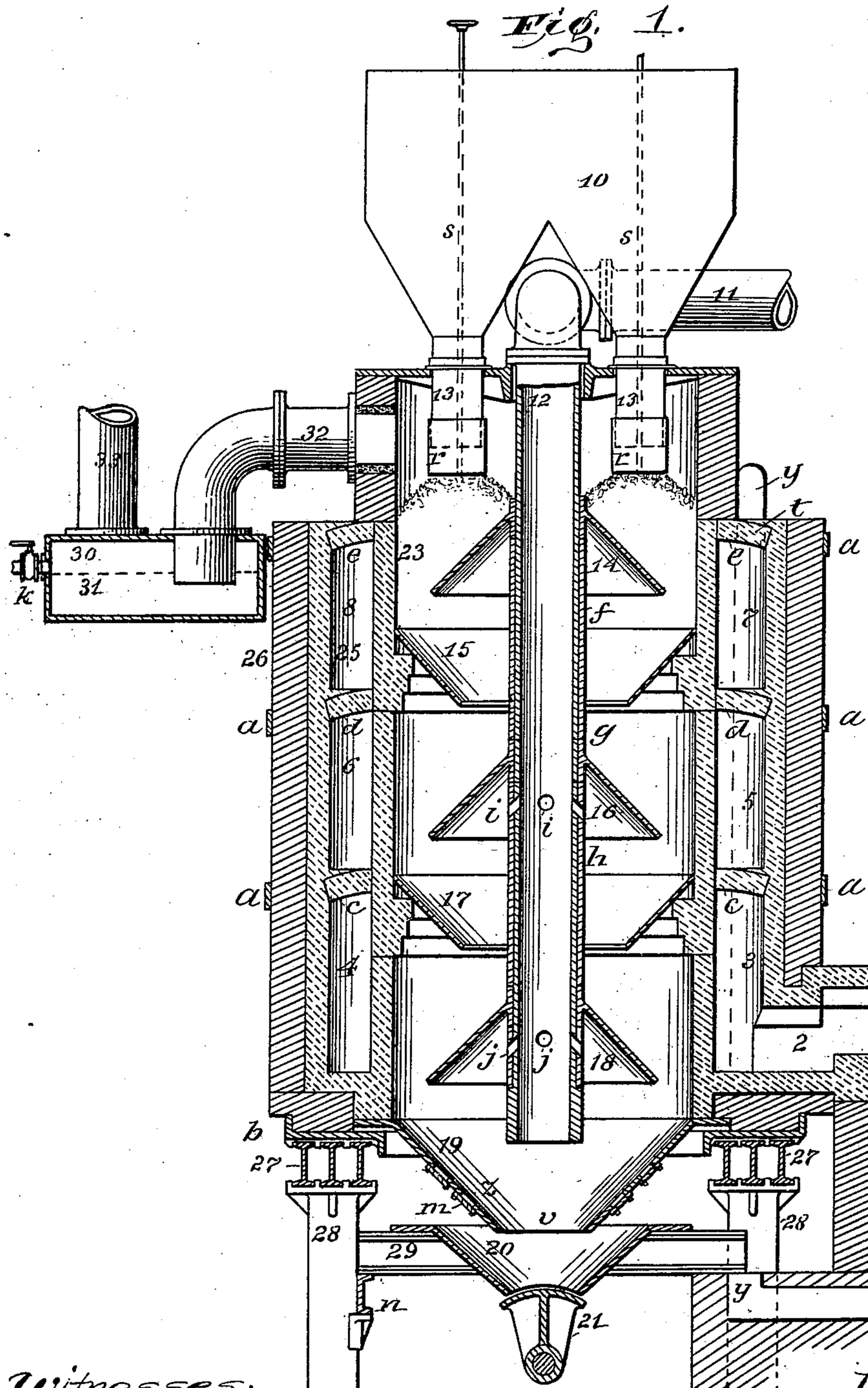
F. GUITERMAN.

ART OF EXTRACTING ZINC FROM ORES.

(Application filed Feb. 14, 1900. Renewed Feb. 11, 1901.

(No Model.) 4 Sheets—Sheet 1.

Fig. 1.



Witnesses:
J. McFowler Jr.
M. J. Dixon

Inventor:
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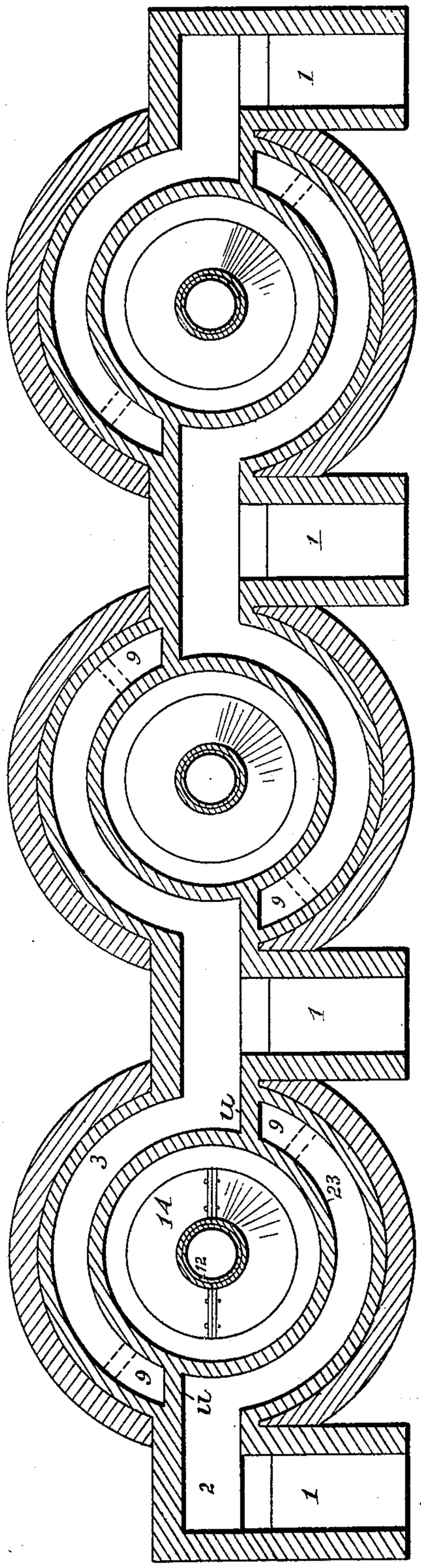
(No Model.) 4 Sheets—Sheet 2.

Fig. 2.



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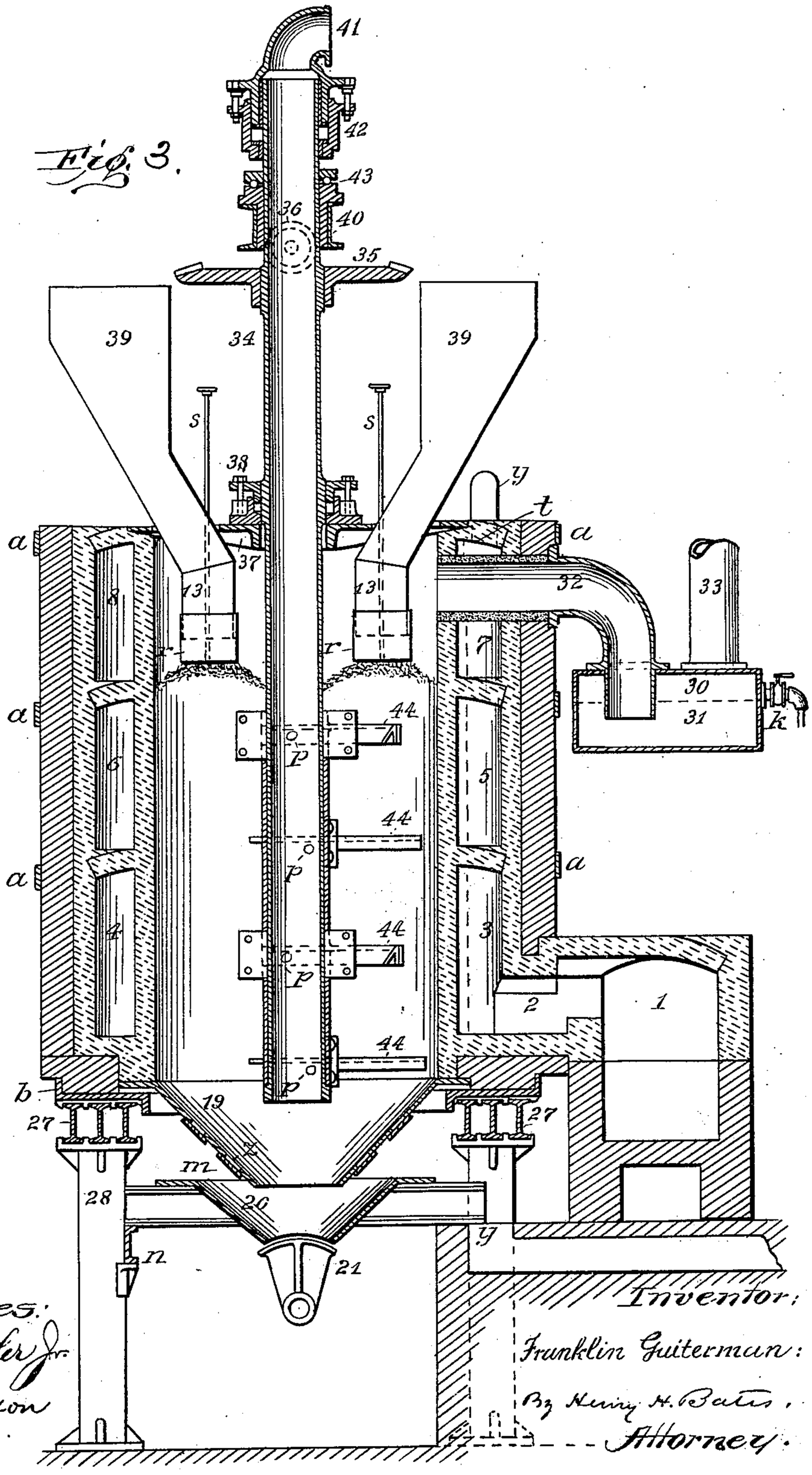
(No Model.) 4 Sheets—Sheet 3.

Fig. 3.



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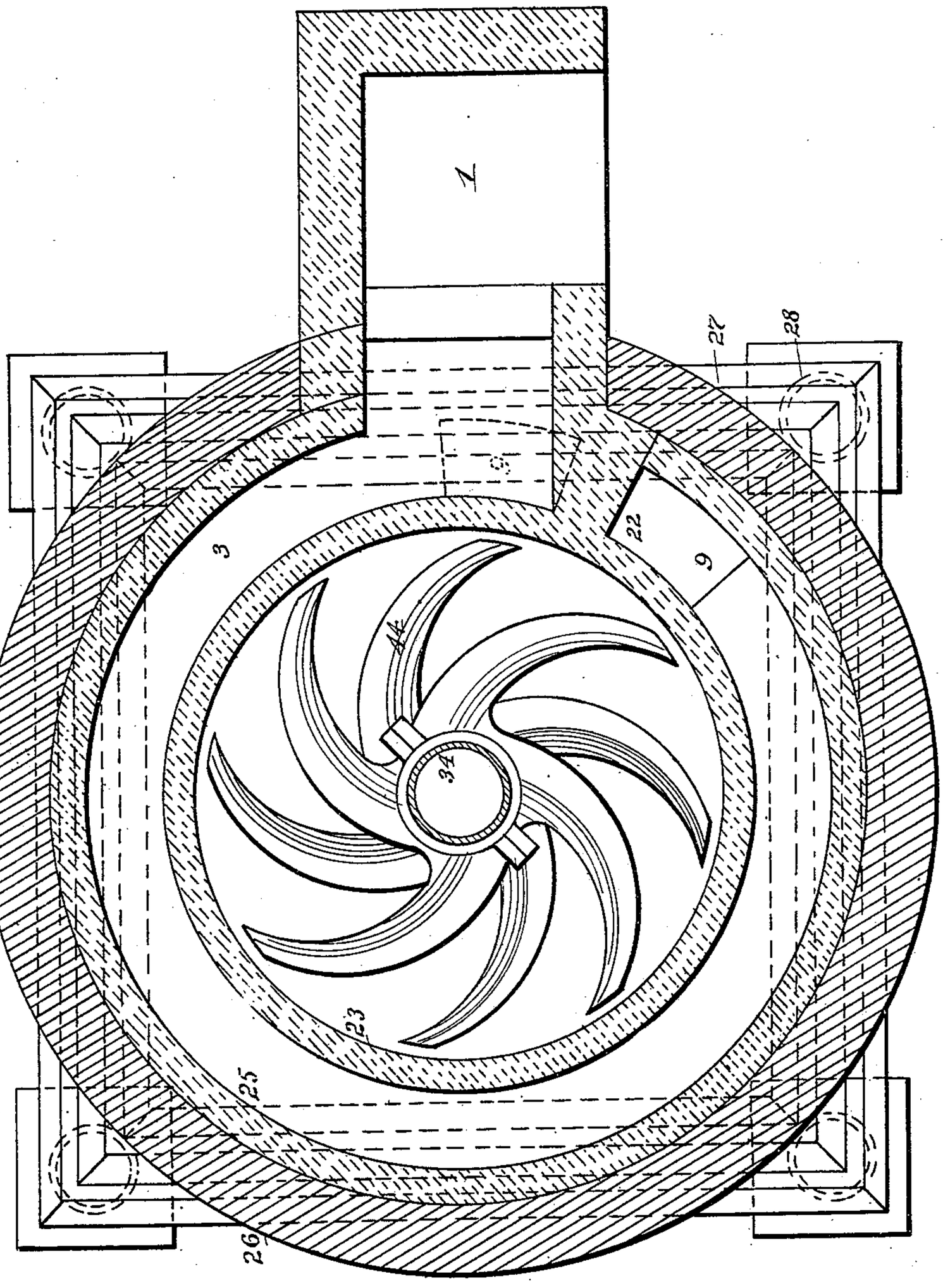

Fig. 4.

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UNITED STATES PATENT OFFICE.

FRANKLIN GUITERMAN, OF DENVER, COLORADO.

ART OF EXTRACTING ZINC FROM ORES.

SPECIFICATION forming part of Letters Patent No. 669,410, dated March 5, 1901.

Application filed February 14, 1900. Renewed February 11, 1901. Serial No. 46,877. (No specimens.)

To all whom it may concern:

Be it known that I, FRANKLIN GUITERMAN, a citizen of the United States, residing at Denver, in the county of Arapahoe and State of Colorado, have invented certain new and useful Improvements in the Art of Extracting Zinc from its Ores; and I do hereby declare the following to be a full, clear, and exact description of the invention; such as will enable others skilled in the art to which it appertains to make and use the same.

My invention relates to the art of extracting zinc from its ores, especially those ores in which zinc is more or less associated with corrosive oxids, such as the oxids of iron or lead, making the treatment by the processes now generally in use expensive and incomplete. The difficulty in treating such ores resides in the fact that both lead and iron oxids when present in marked degree in the zinc ores have exerted a most detrimental influence on the successful carrying out of the zinc-distillation process and on the life of the fire-clay vessels in which the distillation is performed. Again, in the old process a most perfect roast has been necessary as a preparatory step in the treatment of zinc sulfid ores, a roast which can only be obtained by the application of high temperatures and long exposure of the ore to the same. The attendant cost of such roasting has therefore been necessarily high. The mixed sulfid ores of zinc, lead, and iron containing less than forty per cent. of zinc have therefore hitherto been practically unmarketable for the production of spelter. My process therefore especially relates to a preparatory treatment of such zinc ores whereby they are better adapted for the extraction of zinc by the ordinary distillation process in the ordinary zinc retort-furnace. Such ores may be either in a naturally-oxidized state or native sulfids, in which latter case they should first be treated by the ordinary process of roasting to bring them to the oxidized condition.

My improvement consists, essentially, in subjecting such oxidized ores in divided or granular condition in a suitable apparatus for the purpose at a temperature sufficiently high to reduce or partially reduce the iron and lead oxids, but lower than that at which zinc will volatilize to the intimate action of reducing-gases—such as carbonous oxids, hydrogen, hydrocarbon gases, water-gas, natural gas, producer-gas, or any mixtures of the same—in absence of solid reducing agents of any description and with the practical exclusion of atmospheric air or oxygen and all direct action of flame. The said reducing treatment is continued until the iron and lead oxids present are reduced to a metallic state or to that of the lower oxids, a portion of those metals in the form of ferrous and plumbous oxids not being deleterious. As the temperature to which the ore is subjected in the reducing process is not raised to the volatilizing temperature of zinc, the latter metal remains undisturbed. The ore thus prepared is to be withdrawn and subjected to a distillation process at temperatures suitable for ore so treated with the admixture of carbonaceous material, and finally the distilled product is to be properly condensed and cast into ingots. Where silver-lead ores are associated with the zinc ores in considerable amount, such ores, which have heretofore been a positive detriment in the distillation treatment, become of value, since after the recovery of the zinc element the silver-lead metal may be recovered from the residue of the treated ore after the distillation of the zinc by the ordinary processes of lead-silver smelting. In the case of ferruginous zinc ores which have been imperfectly roasted the reduction of the iron in the ore to a metallic state enables said iron in the subsequent operation of distillation of the zinc to disassociate whatever zinc-sulfid compound may remain in the imperfectly-roasted zinc ore, thus permitting a high degree of zinc recovery. Consequently this process thus permits of the utilization of impure ores such as contain iron, lead, arsenic, and antimony compounds to as successful a degree as that of the purer ores. The resulting zinc in such case is much purer than that ordinarily obtained by reason of the volatilization and elimination as vapor of such metals as arsenic and antimony, which if present in the zinc ore are ordinarily retained in the zinc to a large degree, thereby greatly deteriorating its quality.

I have in the accompanying drawings illustrated an apparatus adapted for use in my process, which I will briefly describe in its

essentials before proceeding to the explanation of said process in its details. In such an apparatus it is quite necessary, first, that the heating-flame shall not come in contact with the ore or reducing-gas; second, that the ore shall be delivered to such reducing-gas in divided and permeable form and in a condition of mobility; third, that the ore shall be capable of being heated quite uniformly to a temperature of at least 900° and up to 1,100° Fahrenheit, but not above the volatilizing temperature of zinc, and, fourth, that the reducing-gas shall be capable of delivery to the ore through every portion thereof and under sufficient pressure to exclude atmospheric air or oxygen, which in any considerable quantities would be liable to interfere with and neutralize the necessary chemical reaction.

In the drawings forming a part of this specification, Figure 1 is a vertical section of an apparatus suitable for carrying out my process. Fig. 2 is a plan view, in horizontal section, of a battery of three retorts similar to that shown in Fig. 1. Fig. 3 is a vertical section of a modified form of the apparatus, showing a different means for mobilizing the ore for ores of special character. Fig. 4 is a horizontal section of the apparatus of Fig. 3.

The essentials of the apparatus in both forms illustrated are a vertical retort-cylinder 23, of suitable size, made of refractory material, such as fire-clay, which may be formed in rings of convenient height. Outside of this is a jacket of brickwork 26 at a sufficient distance from the retort to provide for annular passages for the circulation of the hot gases or products of combustion, by which the retort 23 is heated through the walls thereof from the outside. Said jacket is lined with fire-brick or other refractory material 25 and is stayed or bound with hoops of steel *a* where required. The whole structure rests on an annular plate or casting *b*, which is sustained by I-beams 27, resting on the supporting-columns 28, four in number. Arches *c d e*, located at proper intervals, divide the annular space between the two cylindrical walls horizontally into convenient annular chambers or flue-spaces 3 5 7 4 6 8, there being an opening 9 upward through the vault of each annular chamber at one point for the products of combustion to pass through from chamber to chamber, and a barrier-wall *u* being provided in each chamber, as shown, the openings being so located on alternate sides of the said wall as not to come over each other, but cause the flame to make the circuit of each chamber before finding an outlet into the chamber above. A spirally-arranged passage would be the full equivalent of this construction. A fireplace or combustion-chamber is shown at 1, communicating by a flue or throat 2 with the lowermost chamber 3 4. In this combustion-chamber producer-gases are preferably used. The products of combustion escape from the upper chamber through a passage *t* and downtake-flue *y*, which leads to a chimney flue or stack located at some convenient point, through which the hot products of combustion finally escape, the draft being promoted by any of the means in ordinary use.

Centrally within the retort is located and suspended a vertical pipe 12, through which the reducing-gas is introduced to the ore by way of a pipe 11 at the top, leading from a source of supply under pressure. On pipe 12 are conical baffle-plates 14 16 18, held in their proper position by distance pieces or tubes *f g h*, which, with the conical baffle-plates, may conveniently be made in halves for ease of removal or renewal. Said baffle-plates and distance-pieces may be made either of metal, as shown in the drawings, or of fire-clay. Intermediately of the baffle-plates already described are other baffle-plates 15 17, of similar material, suitably supported by the shell 23 of the retort. There are apertures *i j* through the walls of the central pipe and distance-pieces for the passage of gas.

10 is a double hopper communicating with the interior of the retort by conduits 13 13.

r r are movable sleeves mounted on the delivery-tubes 13 13, their position thereon being regulated by means of the rods *s s*, passing up through pipes 13 and hopper 10.

32 is a pipe or passage by which the reducing-gas escapes from the retort after doing its work. It terminates in a water-trap 30, having a water seal 31, an exit-pipe 33, and water-cock *k*.

The lower part of the retort is partially closed by a frusto-conical chute 19, open at *v*, preferably of cast-iron, in which are lateral apertures *z*, closed by removable covers *m*, which apertures serve for the introduction of stirring-bars should the material become agglomerated or adhere. Beneath this chute is a cone or hopper 20, supported by I-beams 29, resting either on pedestals or masonry, as at the right, or on channel-bars and brackets sustained by the columns 28, as at *n*. The lower opening of the hopper 20 is closed by a reciprocating shoe 21, of cast metal, which being moved by suitable power back and forth at the requisite speed, which can be regulated to suit circumstances, permits the reduced ore to fall intermittently into a car or carrier placed beneath.

The construction shown in Figs. 3 and 4 differs in a few details from that already described to serve the treatment of ores which become readily agglomerated, and therefore have to be continually stirred mechanically to prevent agglomeration and give every portion its proper contact with the heating-surface of the retort and with the reducing-gases. To this end I make the central pipe 34 revoluble, supporting it on channel-bars 40 by ball-bearings 43 and connecting stationary pipe 41, which conveys the reducing-gas into the retort, with pipe 34 by means of a stuffing-box 42, so as to make a gas-tight revolving joint. The water-trap 30, outlet-pipe 34, and

exit-pipe 33 are the same as heretofore described. The central pipe 34 has near its point of support a bevel gear-wheel 35, mounted thereon, driven by suitable power through pinion 36 or in other convenient manner, so as to revolve at the requisite speed to do its work. On its circumference are fixed at a suitable distance the radial curved cast-metal arms 44, of an angular cross-section, appearing in Fig. 3. The apertures for the escape of the reducing-gas into the retort are located beneath these arms, in the cavity thereof, as at *p*. The cover 37 has a stuffing-box 38, with asbestos packing, to prevent gases from escaping around the pipe and at the same time permitting the pipe to revolve. The hopper 39 is divided, so as not to interfere with the revolving pipe, or it may be made annular.

The apparatus for the preliminary roasting ore of the sulfid ores and for the final distillation and condensation of the product needs no illustration, being similar to that in common use.

The ores, if sulfids, as before stated, are to be roasted, if necessary, by the ordinary process of treating such ores to bring them to the requisite oxidized condition. The oxidized ores thus obtained, or naturally oxidized ores in granular or divided condition, being charged into the hopper of the apparatus, fall by gravity into the annular space between the wall of the retort and the central pipe. The retort has previously been brought to a high temperature—say from about 900° to 1,100° Fahrenheit—by igniting the fuel in the combustion-chamber (preferably producer-gas) the flame from which passes through the throat 2 into the first annular chamber, making the circuit thereof and passing upward through aperture 9 into the next chamber of the series, and so on, circling around the retort-wall until the products of combustion make final escape through the chimney-flue provided for the purpose. The ore delivered from the hopper, Fig. 1, falls upon the inclined baffle-plate 14, by which it is spread out into a thin layer and deflected toward the heated wall of the retort. Continuing its course by gravity it is again deflected and turned over by the next baffle-plate of the series, and so on throughout its course, by which means it is thoroughly stirred and mixed and made permeable, and all portions thereof receive a proper accession of temperature from the hot walls of the retort with which the ore comes in contact in its descent. The reducing-gas which is to act upon the ore in its heated condition is brought from a suitable containing vessel, being preferably first passed through a water-trap similar to trap 30 and introduced through pipe 11 into central pipe 12, whence it passes through the apertures provided under the baffle-plates and also through the lower outlet of the pipe 12. The gas rises upward through the permeable mass, being supplied under sufficient pressure to penetrate every part. It takes its exit through pipe 32 and water-trap 30, the water seal in said trap being of sufficient head to effect a slight back pressure—say of one or two ounces. The gas may be wasted or conducted around to the fuel-chamber and there burned to utilize the combustible quality contained therein. It is essential that the pressure maintained within the retort should be sufficient to exclude the air from entry, for reasons before explained. The requisite pressure is easily maintained throughout the permeable mass of ore, the retort being designed to be filled with ore up to a regulated height determined by the position of the movable sleeves *r r*. The hopper 10 and the tubes 13 are designed to be kept full of ore, which prevents the gas passing from the retort that way, while at the bottom of the retort the mass of reduced ore accumulated for delivery in the conical shell 19 is both cooler and denser than the permeable mass under treatment and prevents the gas from escaping in that direction, the gas naturally flowing in the direction of least resistance, which is upward through the permeable and settling mass of ore and outward through pipe 32. When the ore is easily agglomerated, so that more efficient means for stirring it than the baffle-plates above referred to become necessary, the mechanical treatment is varied in the way illustrated in Figs. 3 and 4. The revolving stirrers carried on the revolving pipe 34 are then brought into use, the treatment being otherwise in all respects similar to that above described. When a battery of several retorts is made use of, as illustrated in Fig. 2, I prefer to locate a fireplace or combustion-chamber between each pair of retorts and also one at each end of the battery, so as to admit the hot products of combustion at two opposite points of each retort instead of one, as in the case above described. The flame thus makes but a half-circuit for each supply, two uptake-passages 9 being provided instead of one. Any desired number of retorts may be arranged in a battery, three being shown as sufficient for illustration. The ore having been sufficiently treated by the action of the reducing-gases to bring the lead and iron oxids contained in such ores wholly or partially to the metallic state, the remainder being in the state of lower oxids, the ore is intermittently withdrawn at the base of the apparatus by means of the reciprocating shoe above described or in any other convenient manner, whence it is conveyed away to the distilling apparatus to be subjected to the step of distillation at a temperature sufficient to drive off and recover the zinc in metallic form, which under this method of treatment will take place at a much lower degree of temperature than is required in the usual processes and with a larger yield. The zinc is also of purer quality, since the more volatile metals—such as arsenic and antimony, the presence of which in the zinc deteriorates its

quality—are driven off in the preparatory process. After distillation the lead and precious metals, which may be present to a valuable extent in the ores under consideration, can be recovered from the residue in which they remain by the ordinary processes of silver-lead smelting.

The lower part of the apparatus in which the reduction takes place being below the heating zone and formed of a thin metallic shell becomes a cooling area, so that the hot ores which have been treated and have subsided to that point become cooled to a degree where there is no danger of reoxidation after discharge from the apparatus. Besides, in the practical carrying out of this process the ore will ordinarily be discharged into some means of conveyance to a distant point for distillation, in which the ore may be at once mechanically mixed with the carbonaceous material necessary to be used in the distilling process, which carbonaceous material will in itself tend to prevent any reoxidation of the reduced oxids.

I claim and desire to secure by Letters Patent—

1. The process of extracting zinc from its oxidized ores containing corrosive metallic oxids, which consists in introducing the oxidized ore in a divided or granular condition into a receptacle, heating the said ore through the walls of said receptacle, to a high temperature but below the volatilizing temperature of zinc, maintaining said ore in a permeable and mobile condition during the operation of heating, introducing into intimate contact with said ore a current of reducing-gas, under pressure, throughout the heating, continuing the heating and the action of the reducing-gas until the corrosive metallic oxids are reduced as described, withdrawing said ore and finally recovering the metallic zinc therefrom by distillation, substantially as specified.

2. The process of extracting zinc from its ores which consists in, first, roasting the sulfid ore to oxidize the same; second, introducing the oxidized ore in a divided or granular condition to the action of heat while shielded from contact with flame or atmospheric air; third, maintaining said ore in a permeable and mobile condition during the operation of heating; fourth, introducing into intimate contact with said ore a current of reducing-gas, under pressure, throughout the heating, continuing the heating and the action of the reducing-gas until the corrosive metallic oxids are reduced as described; fifth, withdrawing said ore and finally, sixth, recovering the metallic zinc therefrom by distillation, substantially as specified.

In testimony whereof I affix my signature in presence of two witnesses.

FRANKLIN GUITERMAN.

Witnesses:
MARY B. GUITERMAN,
RICHARD FULLER.