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Griffith et al.

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[54] **METHOD FOR TREATING COPPER ORE CONCENTRATES**

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[51] **Int. Cl.** **C22b 1/10; C22b 15/00**
[58] **Field of Search** 75/3, 9, 1, 26, 72, 74

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[57] **ABSTRACT**

Method and apparatus for oxidizing mixed solids containing copper compounds and other metal sulfides by heat treatment to produce a calcine having the copper compounds in readily leachable form and these other metal sulfides in a difficulty leachable form in which the mixed solids are roasted by passing through two successive fluid bed roasters. The gaseous products and entrained solids from each roaster are separated and the separated solids recycled through the second roaster for further roasting.

8 Claims, 4 Drawing Figures

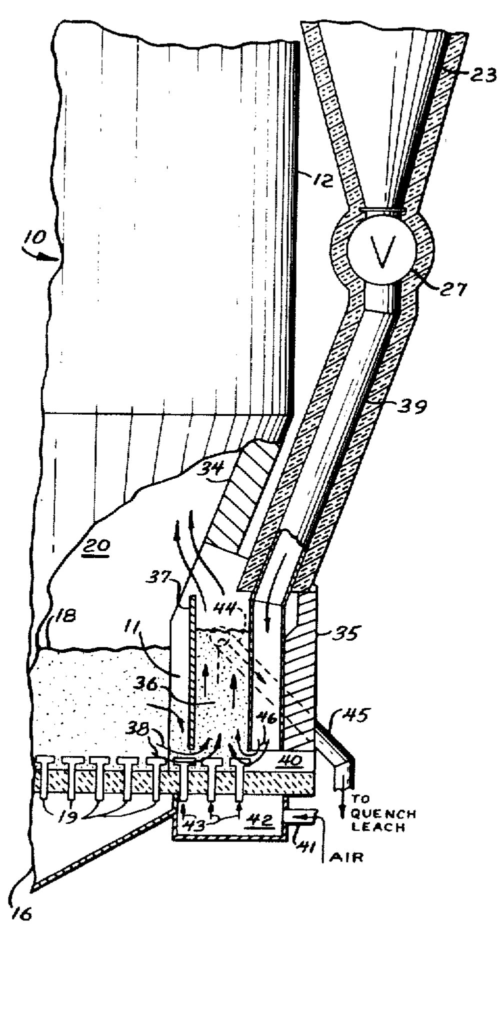


Fig. 1 PRIOR ART

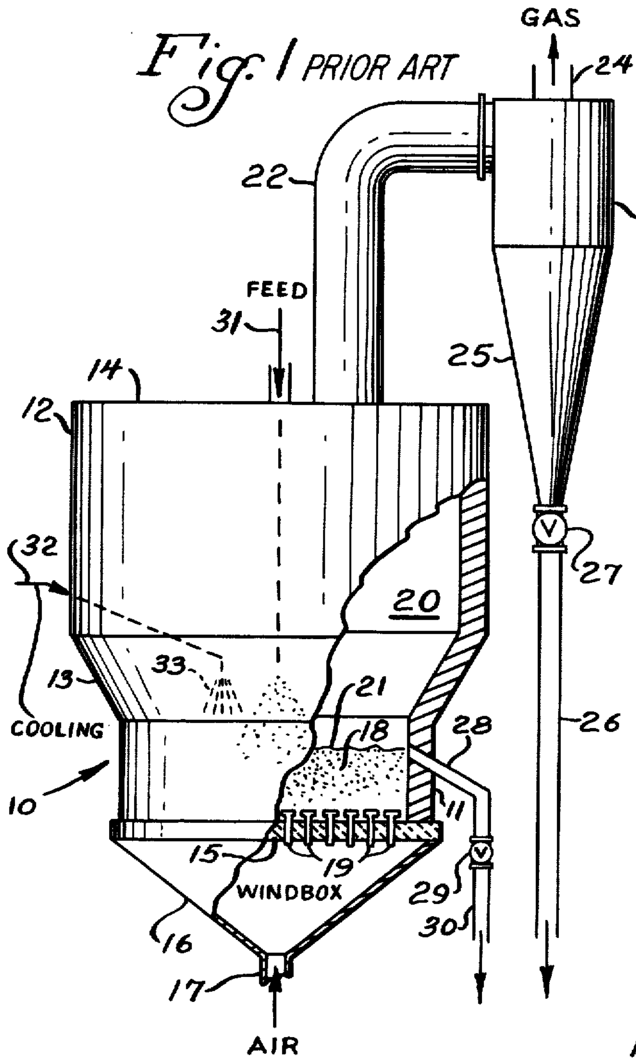
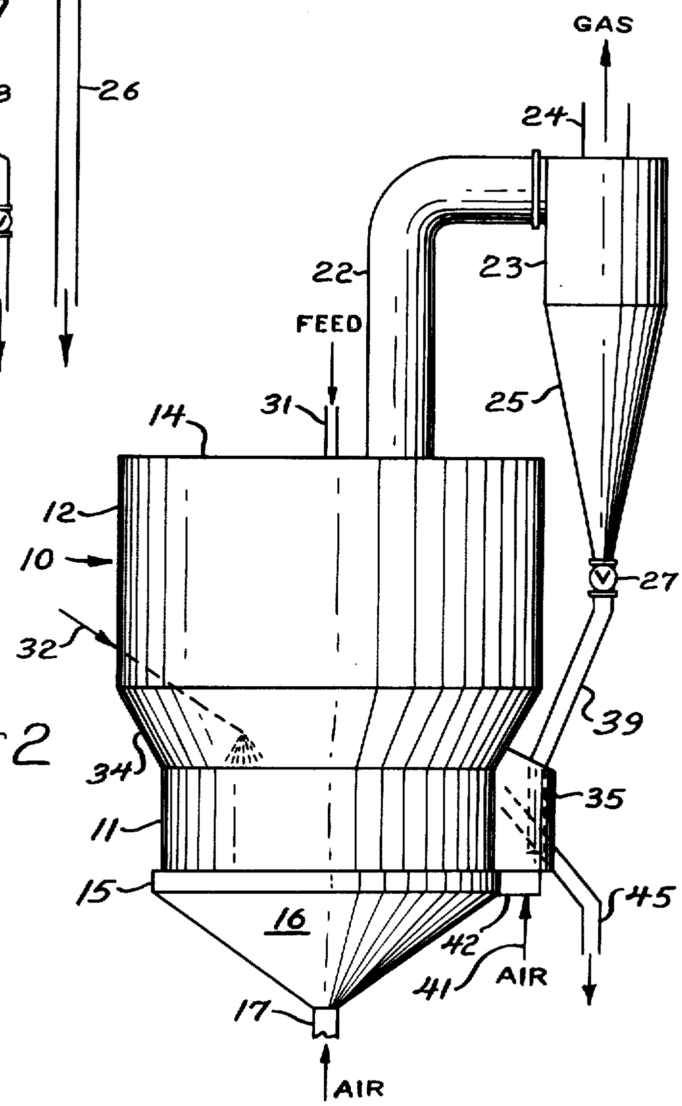
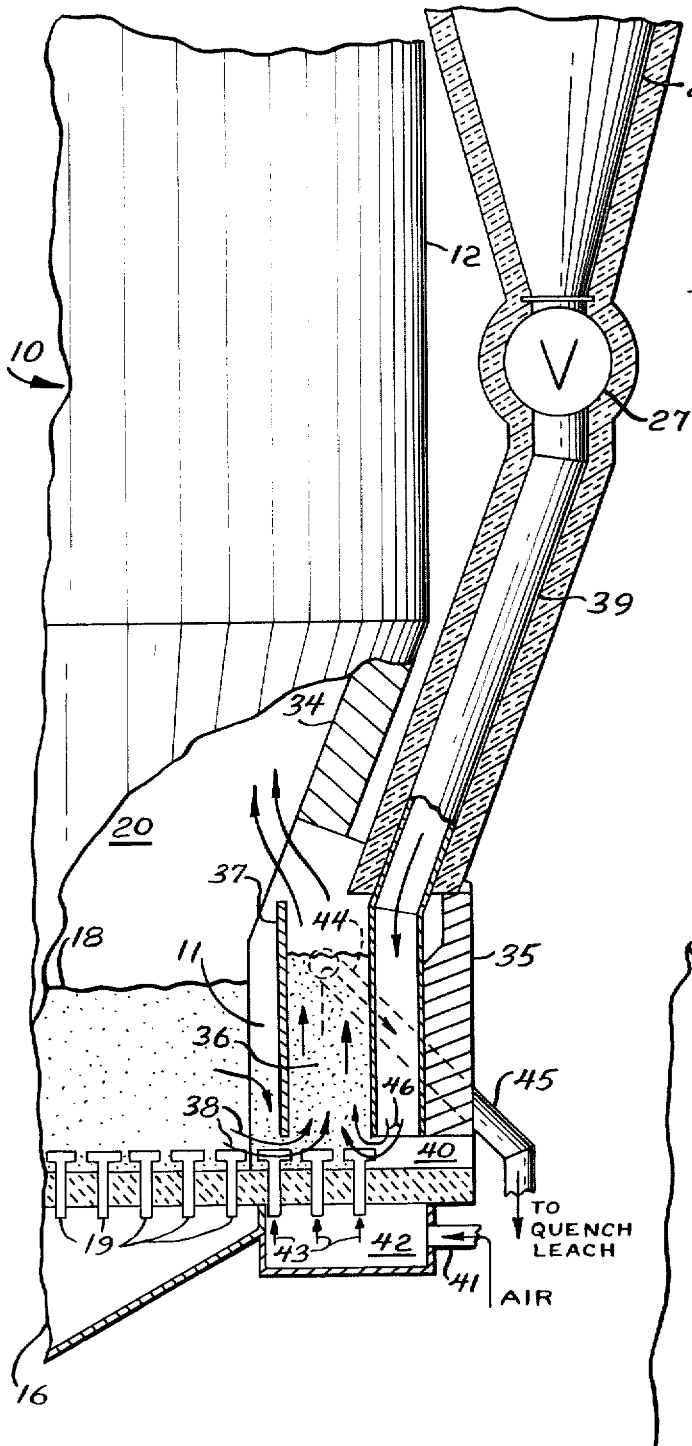


Fig. 2




23
12
10
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34
20
37
44
18
11
35
36
38
46
45
40
19
43
42
41
TO QUENCH LEACH
AIR
16

Fig. 3

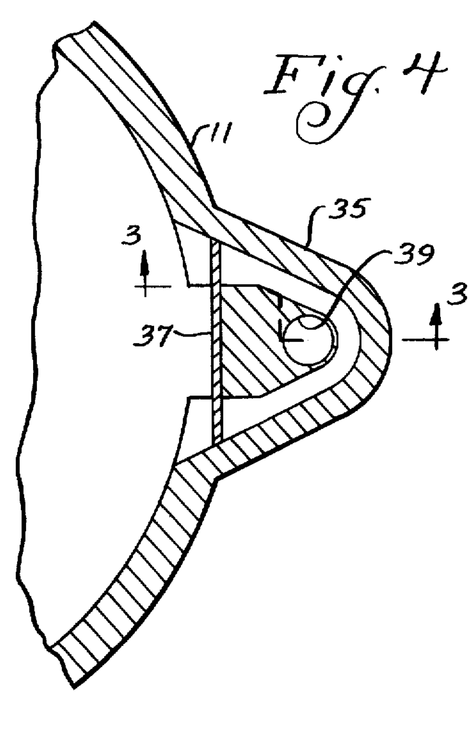
11
35
3
39
3
37

Fig. 4

METHOD FOR TREATING COPPER ORE CONCENTRATES

BACKGROUND OF THE INVENTION

The field of the art to which the invention pertains is in the selective roasting of ores or concentrates containing copper compounds in association with sulfidic materials, including metal sulfides and particularly iron sulfide, in which the copper is converted to primarily soluble copper compounds while the other metal sulfides are converted to products that are primarily insoluble. The resulting calcine product can then be easily and efficiently leached to extract the soluble copper compounds while leaving the other components in the calcine.

The most pertinent prior art of which applicants are aware are U.S. Pat. No. 2,783,141 and the article "Bagdad Reports Metallurgical Test Results on Copper Recovery Method" published in Engineering and Mining Journal for July, 1957, pages 86–89.

Although the methods and apparatus described in this prior art are generally concerned with the same problems as is the present invention, the methods and apparatus described and claimed herein have advantages which will be described in detail hereinafter which are not present in this or any other prior art of which applicants are aware.

SUMMARY OF THE INVENTION

In general the method and apparatus of this invention involve roasting the finely divided mixed solids containing the copper compounds and other metal sulfides in two successive fluid beds and in the presence of free oxygen which may be from air to produce an oxidized bed comprising copper sulfate which is readily leachable and with gaseous reaction products being separated from the solids at an intermediate point between the two beds.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a side elevational view partially in section illustrating an apparatus and method of the prior art.

FIG. 2 is a side elevational view of an apparatus embodying the invention.

FIG. 3 is an enlarged sectional detail of a portion of the apparatus of FIG. 2 with the section taken substantially along line 3—3 of FIG. 4.

FIG. 4 is a horizontal section through a portion of the apparatus.

DESCRIPTION OF THE PREFERRED EMBODIMENT

It is generally known to roast mixed solids containing copper compounds and other metal sulfides to produce a calcine having the copper compounds in a readily leachable form and the other metal sulfides in a difficulty leachable form by reacting the compounds including the sulfides in a fluid bed reactor with free oxygen, removing the roasted calcine products from the fluid bed reactor and leaching with a liquid to remove the soluble copper compounds from the resulting calcine. Thus the converting of the copper to soluble form by fluidized roasting techniques is generally old in which the finely divided solids are fluidized in an upward moving stream of gas that contains free oxygen. The partially suspended solids behave much like a liquid and the mass boils and bubbles similar to boiling water, seeks its own level like a liquid and overflows into a pipe or the like that serves as a transfer conduit. Such a fluidized mass of finely divided solids has a low apparent density and the top of the fluidized bed has a sharp separation from the gas space above.

FIG. 1 illustrates a form of apparatus used in the prior art roasting of mixed solids as described above and with the apparatus of the present invention being a modification of this prior apparatus. Similarly, the method of this invention is a modification of the prior art method. Because portions of the prior art apparatus of FIG. 1 are similar to those of the present invention as shown in FIGS. 2, 3 and 4 the same numerals will be used to identify similar parts both in FIG. 1 and in FIGS. 2–4.

In the apparatus of FIG. 1 there is illustrated a single bed reactor or roaster **10** with a generally cylindrical insulated side retaining wall **11**, an enlarged cylindrical insulated wall **12** above it and connected at the bottom to the top of the wall **11** by an outwardly flared insulated wall portion **13** with the top of the upper cylindrical wall **12** being closed by a fluid tight end **14**.

The bottom of the cylindrical wall **11** is separated by a horizontal insulated plate from a bottom wind box **16** to the bottom of which is supplied air under pressure through a centrally located pipe **17**.

The cylindrical wall **11** above the horizontal plate **15** describes a fluidized bed zone in which are located the particles of finely divided mixed solids comprising the fluid bed **18**.

Fluidized roasting is achieved by supplying air or other gases containing free oxygen that is available for oxidation through the pipe **17** into the wind box **16** and into the lower areas of the bed **18** by means of adjacent tuyeres **19** extending vertically through the plate **15** and with their lower ends opening into the wind box **16** and their upper ends discharging transversely into the loose particles of the fluid bed **18**.

During the operation of the apparatus of FIG. 1 as well as the present invention the upward passage of the air, the fluidizing of the bed **18** and the reaction within the bed causes a gaseous mixture of air, gaseous reaction products and fine dust to pass upwardly through the gas space **20** in the reactor **10** above the top surface **21** of the fluid bed **18**.

A large diameter pipe **22** that extends from the top end **14** of the reactor leads to a gas separator here embodied in the cyclone separator **23** which is of customary construction and in which the entrained solids are separated from the gas which passes out a top pipe **24** and with the separated solids being directed by a conical bottom **25** of the separator **23** to a discharge pipe **26** by way of a rotary air lock valve **27**.

In the prior art apparatus of FIG. 1 the roasted calcine product from the bed **18** is drawn off from the top **21** of the bed through a discharge pipe **28** also provided with a rotary air lock valve **29** similar to the valve **27**. Both the fluid bed overflow from the valve **29** through the discharge pipe end **30** and the solids from the cyclone underflow through the discharge pipe **26** are constructed to a place of copper separation where the calcine is leached to remove the soluble copper and the separated copper is further purified as by precipitation of the copper by electrolysis. As the leaching and electrolytic purification are conventional and well known they are not shown.

As the roasted calcine product is withdrawn fresh feed is provided in the form of a slurry through a feed pipe **31** in the top end **14** of the reactor **10** so that the slurry falls through the heated gas space **20** onto the top **21** of the fluidized bed **18.** In addition, in order to control the temperature a cooling medium such as water is supplied by automatic controls which likewise are conventional and not shown through a cooling supply pipe **32.** The customary cooling medium is water which is sprayed as indicated at **33** onto the top **21** of the fluidized bed **18.**

The amount of air or similar free oxygen containing gas that is supplied by way of the wind box **16** and pipe **17** is in sufficient excess to convert the copper sulfide to water soluble copper sulfate. In addition, the temperature in the fluid bed **18** is accurately regulated to preferably about 550°–750°C. with the temperature being kept from becoming too high by the cooling medium supplied by the pipe **32.** If the roasting temperature is too low the other metal sulfides in the mixed solids of the bed **18** including iron will be solubilized so that they will be leached from the calcine with the desired copper. If the temperature of roasting in the bed **18** is too high a portion of the copper will be rendered insoluble and thus will not be removable in the subsequent leaching. In order to maintain a desired maximum temperature the supply of cooling medium such as water through the pipe **32** is automatically controlled by well known means that are not shown.

The slurry containing the suspended solids that are fed to the reactor as through the feed pipe **31** is prepared in the customary manner (not shown) in which the finely divided feed solids are pulped in water and then pumped to the reactor through the pipe **31.**

In the usual equipment as illustrated in FIG. **1** the gas that is discharged from the separator **23** through the pipe **24** is treated by passage through gas scrubbers (not shown) before being ejected through a customary stack.

The velocity of the upwardly passing air through the fine solids of the reactor bed **18** is sufficient to maintain the fluidization of these solids as explained above and is customarily at a velocity of about 1 to 2 feet per second. This is sufficient to maintain the bed in fluidized condition, to cause the free oxygen to react with the fluidized particles and to force the gases from the bed **18** carrying the fine solids into the gas or freeboard space **20.** In this space some of the larger particles fall back into the bed **18** with the very fine particles or dust passing with the gas through the pipe **22** into the separator **23** as previously described.

The air supply and pressure and the temperature of the reactor bed **18** are interrelated as is well known in this art and as is discussed fully in the above prior art patent.

The air supply into and through the wind box **16** is in excess of the theoretical amount of oxygen necessary to complete the desired reactions in the bed **18.** This stoichiometric amount of oxygen is that sufficient to convert the metals to the oxides and the sulfur to sulfur dioxide and to convert substantially all of the copper present to copper sulfate. The chemical reactions that take place in the reactor of this invention are many and varied but the more important reactions are as follows:

1.	$Cu_2S + 2O_2$	$\rightarrow$	$2CuO + SO_2$
2.	$4CuFeS_2 + 13O_2$	$\rightarrow$	$4CuO + 2Fe_2O_3 + 8SO_2$
3.	$4FeS_2 + 11O_2$	$\rightarrow$	$2Fe_2O_3 + 8SO_2$
4.	$2SO_2 + O_2$	$\rightleftarrows$	$2SO_3$
5.	$CuO + SO_3$	$\rightleftarrows$	$CuSO_4$
6.	$Fe_2O_3 + 3SO_3$	$\rightleftarrows$	$Fe_2(SO_4)_3$
7.	$2FeS_2 + 5O_2$	$\rightarrow$	$2FeO + 4SO_2$

As indicated earlier, the reactions taking place in the reactor are very temperature sensitive. Thus higher roasting temperatures favor the formation of relatively insoluble oxides of the metals including those of copper and iron. On the other hand, the lower roasting temperatures increase the amounts of relatively soluble sulfates including copper and iron. The results are that if the temperatures are too high there is greater difficulty in leaching copper from the resulting calcine. On the other hand, if the temperature is too low the copper is easily leached as it is in the form of copper sulfate but it is contaminated with iron sulfate and the like which is also easily leached. It is therefore necessary to control the temperature under conditions such that substantially all of the copper is converted into the easily soluble form while substantially none of the other metals including iron are so converted.

In the method and apparatus of this invention as illustrated by the embodiment of FIGS. **2–4** the reactor **10** comprises the side retaining wall **11,** the upper cylindrical wall **12,** the flared wall portion **34,** the end wall **14,** the horizontal plate **15** on which is supported a fluid bed **18** that is supplied with air as by the spaced tuyeres of the type illustrated at **19** and an upper gas space or freeboard **20.**

The reactor **10** in FIG. **2** is also provided with the gas discharge pipe **22** discharging to a separator **23** from which leads the gas exhaust pipe **24.** This separator **23** which is shown is a cyclone is also provided with the inverted conical bottom **25** that is closed by the rotary air lock valve **27.**

In the illustrated embodiment of the invention the bottom of the reactor in the vicinity of the edge of the main bed **18** is in communication with an outwardly projecting wall portion **35** that is also insulated and that defines a secondary bed zone **36** in which is maintained a secondary fluidized bed. The secondary bed is separated from the main bed **18** by a heat conducting wall which as shown is a metal baffle **37.** This baffle **37** has a bottom spaced above the supporting plate **15** so that the calcine material from the main bed **18** may pass through a bottom passage **38** beneath the bottom of the baffle **37** into the secondary bed **36.**

The separated very fine solids or dust from the cyclone separator **23** that flow through the valve **27** are conveyed by a discharge pipe **39** downwardly within the insulated wall portion **35** to adjacent the bottom of the secondary bed **36** where it contacts the top of the horizontal plate **15.** These separated dust particles as illustrated by the arrows **46** flow laterally through a bottom passage **40** into the bottom of the secondary bed **36** and upwardly comingled with the roasted calcine material from the main reactor bed **18.**

In the secondary bed **36** the mixed finely divided solids from the primary bed **18** and the separator **23** are supplied with their own fluidizing air through a pipe **41** into a small wind box **42** and upwardly into the secondary bed **36** through tuyeres **19** as indicated schematically by the arrows **43.** Further reaction takes place in this secondary bed **36** and the overflow calcine from the fluidized bed leaves the top **44** of this bed through the discharge pipe **45** for leaching separation of the copper sulfate and electrolytic purification of the copper as previously described.

The fine particles carried upwardly through the gas space **20** above the first or primary fluidized bed **18** may constitute 40–70 percent of the total solids discharged from the roaster through the discharge pipe **45.** These very fine particles or dust have a short retention time in the roaster as they are carried along rapidly by the upwardly flowing air and gas stream and thus are incompletely roasted and contain unroasted sulfides of the metals including those of copper and iron. In addition, the slow cooling of the fine particles in the dust collectors of both the prior art FIG. **1** and the apparatus of this invention results in increasing amounts of undesirable soluble and therefore leachable iron sulfate rather than the desired insoluble iron and similar metal oxides. As a result the separated dust product contains relatively less soluble copper and relatively more soluble iron than the bed overflow product as illustrated by that flowing through the discharge pipe **28** of the FIG. **1** prior art apparatus.

These results are proven by the following data in which the calcine overflow from the reactor bed **18** through the discharge pipe **30** was collected and the cyclone **23** underflow through the discharge pipe **26** was collected separately. The copper and iron solubilities were determined by a standard leach test with the following results:

	Bed Overflow	Cyclone Underflow
Soluble Copper	95.5%	73.7%
Soluble Iron	6.4%	20.5%

Applicants have discovered that the solution to this problem where the entrapped dust that is separated in the separator is incompletely roasted is to recycle the dust through a fluidized bed roaster in such a way that its temperature is maintained at a high level, the dust is given additional reaction time and the agglomeration of the dust with the coarser finely divided solids from the main bed is promoted. Furthermore, the entire roaster product of calcine which is discharged through the single discharge pipe **45** is cooled quickly by quench leaching by conveying immediately to a calcine quench tank in the manner illustrated in the above prior art journal article.

The additional fluidizied air supplied to the secondary fluidizing bed **36** by way of the wind box **42** is supplied generally under the same conditions as the air supply to the main reactor bed **18** through the pipe **17.** This fluidizing air into the bed **36** promotes additional oxidation of the sulfides that have not yet been oxidized and particularly those in the separator dust and also aids in mixing the dust flowing into the secondary bed **36** through the passage **40** and the coarser main bed **18** particles flowing through the passage **38.** This allows additional time and additional oxygen for reactions including those listed at **1** thru **7** above to continue. The temperature in the secondary bed **36** reactor is maintained close to the temperature of the main bed reactor **18** with the difference in temperature being not greater than about 100°C. and in some instances the temperature difference is zero which means that the reaction temperatures in both beds **18** and **36** are substantially the same. This is accomplished by insulating the cyclone **23** and associated parts **25** and **39** to minimize heat loss, by heat supplied by the flow of solids from the main bed, by heat conducted to the secondary roaster bed **36** through the single metal baffle **37** and by heat generated by the continuing oxidation reaction in the secondary bed **36.**

The coming together of the coarser particles from the main bed **18** and the fine particles from the separator dust in the secondary bed **36** causes a partial agglomeration of the two in the secondary bed with the result that build-up of a high circulating load is avoided. Then, as mentioned above, the mixed cyclone and main bed **18** products from the secondary bed **36** are discharged directly through the overflow pipe **45** into the leach tank (not shown) so that slow cooling is avoided and the cooling is, in contrast, quite rapid.

In practicing the method of this invention and operating the illustrated apparatus air is supplied to main bed **18** through pipe **17** and to the secondary bed **36** through pipe **41.** The secondary bed air of course is not supplied until there is sufficient solids in the secondary bed. The reaction in the bed **18** is started by introducing a fuel and igniting it both by apparatus that is not shown as they form no part of the present invention. The fuel supply is continued until the reactor bed **18** reaches the desired reaction exothermic temperture at which time the slurry feed **31** is started. The air rising up through the beds maintains them in the above described fluidized condition. When necessary to maintain the desired reaction temperature, as explained above, a cooling liquid such as water is supplied automatically by means not shown through the supply pipe **32.**

The very fine solids or dust carried upwardly through the space **20** are separated from the gas in the separator cyclone **23** and are then fed downwardly and laterally through the passage **40** into the bottom of the secondary bed **36** for further reaction, as described, and the substantially completely reacted calcine product is discharged through the overflow pipe **45.**

As can be seen from the above description the fine solids carried upwardly with the gaseous material from both beds **18** and **36** are recirculated through the second bed **36** where they receive the additional heat treatment as described for further conversion of copper insoluble compounds into soluble compounds for subsequent leaching and for converting the other metals and particularly iron from soluble compounds into insoluble compounds. This recirculation of the very fine solids that are entrapped in the flowing gases not only produces this additional and more complete heat treatment but also causes these fine solids to agglomerate with the larger particles from the main bed **18.** The result is that most of the fine and previously gas entrapped solids are discharged from the roaster in the calcine flowing through the discharge pipe **45.**

The following two examples show the increased copper solubility and decreased iron solubility obtained as a result of operation with a secondary roaster. For both example, a copper concentrate analyzing approximately 25% copper, 25% iron and 31% sulfur was mixed with water (70% concentrate with 30% water) and fed to a 2-foot diameter fluid bed roaster. In test number 1012 the cyclone underflow and primary roaster bed overflow products were collected separately and the copper and iron solubilities determined by a standard leach test. The weighted average copper and iron solubilities for the entire roaster discharge were calculated. In test number **1014** the cyclone underflow was returned to the secondary roaster along with the roaster overflow and the mixture in the secondary roaster was fluidized at a temperature of 640°C. The operating conditions and copper and iron dissolutions are shown in the following table:

	Test 1012	Test 1014
Bed temperature, °C.	685	685
Space rate, ft./sec.	2.0	2.0
Pounds/min. of sulfur in concentrate feed/pounds/min. of fluidizing air	0.11	0.11
% copper dissolved		
Bed overflow	95.5	
Cyclone underflow	73.7	
Total	88.2	93.9
% iron dissolved		
Bed overflow	6.4	
Cyclone underflow	20.5	
Total	11.4	8.6

By using the secondary roaster as described in this invention the copper dissolved was increased from 88.2 to 93.9 percent while the iron dissolved was decreased from 11.4 to 8.6 percent.

Two additional examples serve to show the improvement attained by maintaining the secondary roaster temperature close to the primary roaster temperature. In test number **15** the secondary roaster temperature was 495°C., 206°C. below the primary roaster bed temperature, and in test **33** the secondary roaster temperature was 630°C., 71°C. below the primary roaster bed temperature. The operating conditions and copper and iron solubilities are shown in the following table:

	Test 15	Test 33
Concentrate feed		
% copper	25.8	26.1
% iron	26.8	23.8
% sulfur	28.7	29.8
% solids	65	69
Bed temperature, °C.	701	701
Secondary roaster temperature, °C.	495	630
Space rate, ft/sec	2.0	1.78
Ratio - Sulfur in feed/fluidizing air	0.095	0.105
% copper dissolved	96.1	97.6
% iron dissolved	4.8	3.8

As a result of increasing the secondary roaster temperature to within 71°C. of the primary roaster bed temperature, copper solubility increased from 96.1 to 97.6 percent and iron solubility decreased from 4.8 to 3.8 percent.

As is shown principally in FIG. **3** the separator **23** and the pipe **39** leading from the bottom of the separator to the secondary bed or reactor **36** are insulated as shown against substantial heat losses so that the separated material directed into the bottom of the secondary reactor **36** is at an elevated temperature by the time it reaches the reactor.

Also as indicated in FIG. **3** the calcine from the discharge pipe **45** is directed to a quench leach in the manner shown and described in the above noted article in the Engineering and Mining Journal.

Having described our invention as related to the embodiments set out herein, it is our intention that the invention be not limited by any of the details of description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the appended claims.

We claim:

1. The method of oxidizing metal solids containing copper compounds and other metal sulfides to product a calcine having the copper compounds in a readily leachable form and said other metal sulfides in a difficulty leachable form, comprising: maintaining said solids in a finely divided form in a loose, flowable main bed while contacting the solids with a supply of free oxygen and maintaining said bed at an elevated temperature of about 550°–750°C. to produce an oxidized bed comprising copper sulfate and gaseous reaction product mixed with entrapped fine solids; isolating said gaseous reaction products mixed with said fine solids from said main bed; separating said entrapped fine solids from said gaseous reaction products exteriorly of said main bed while maintaining an elevated temperature in said fine solids and then mixing said heated fine solids after said separating with a portion of the 550°–750°C. solids from said main bed to form a mixture of finely divided solids; maintaining said mixture of finely divided solids in a loose, flowable secondary bed while contacting the solids in said secondary bed with a separate supply of free oxygen substantially at the location where said mixing of said separated fine solids and said main bed portion occurs and maintaining said secondary bed at a roasting temperature of about 450°–750°C., said secondary bed temperature being not more than about 100°C. below that of said main bed to product a calcine rich in copper sulfate; and discharging said secondary bed calcine preparatory to recovering the copper content.

2. The method of claim **1** wherein said solids are subjected in said beds simultaneously to said separate flows of free oxygen under pressure to maintain said loose flowable beds.

3. The method of claim **1** wherein said gaseous reaction products and entrapped solids are conveyed from the vicinity of said main bed to a separator, followed by separating said entrapped solids and conveying the separated solids to said secondary bed for said mixing.

4. The method of claim **1** wherein said secondary bed is maintained in heat receiving contact with the main bed to receive heat therefrom.

5. The method of claim **4** wherein both said main and secondary beds are insulated against substantial heat losses to the external ambient environment.

6. The method of claim **1** wherein said solids are subjected in said beds to a flow of gas that contains the free oxygen with the gas being under pressure to maintain said loose flowable beds and conveying said gaseous re-

action products and entrapped solids from the vicinity of said main bed to a separator, separating said entrapped solids and conveying the separated solids to said secondary bed for said mixing.

7. The method of claim **6** wherein said secondary bed is maintained in heat receiving contact with the main bed to receive heat therefrom and said main and secondary beds are insulated against substantial heat losses to the external ambient environment.

8. The method of claim **3** wherein said separator is insulated against substantial heat losses and said separated solids are insulated against substantial heat losses during said conveying.

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