

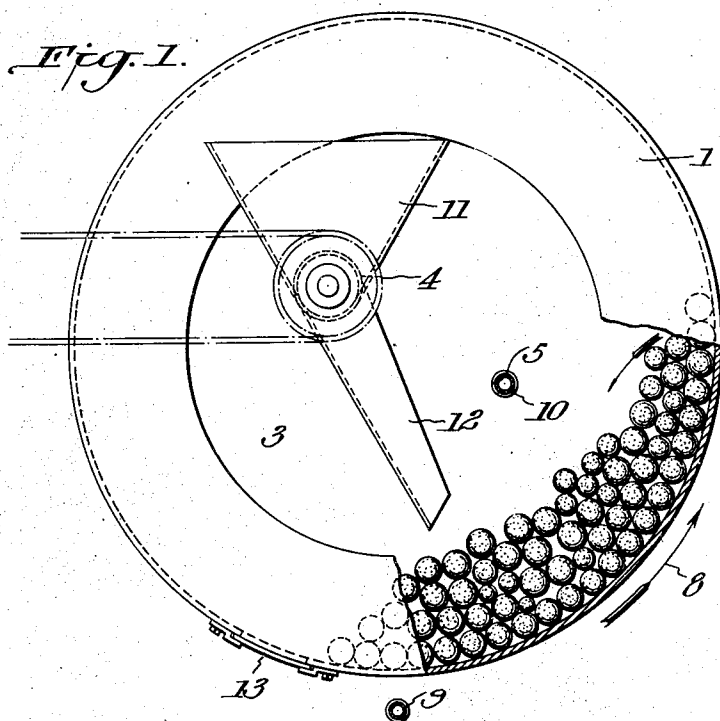
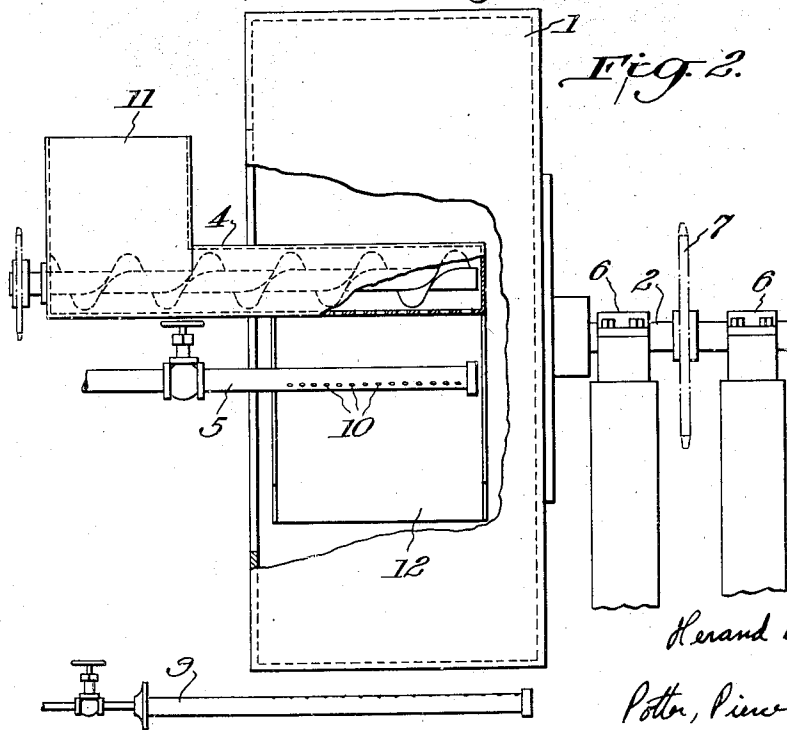
Aug. 23, 1938.

H. K. NAJARIAN
CONCRETIONARY AGGLOMERATE

2,127,632

Filed May 8, 1935

3 Sheets-Sheet 1



Inventor

Herand K. Najarian
Potter, Pines & Scheffer
Attorneys.

Aug. 23, 1938.

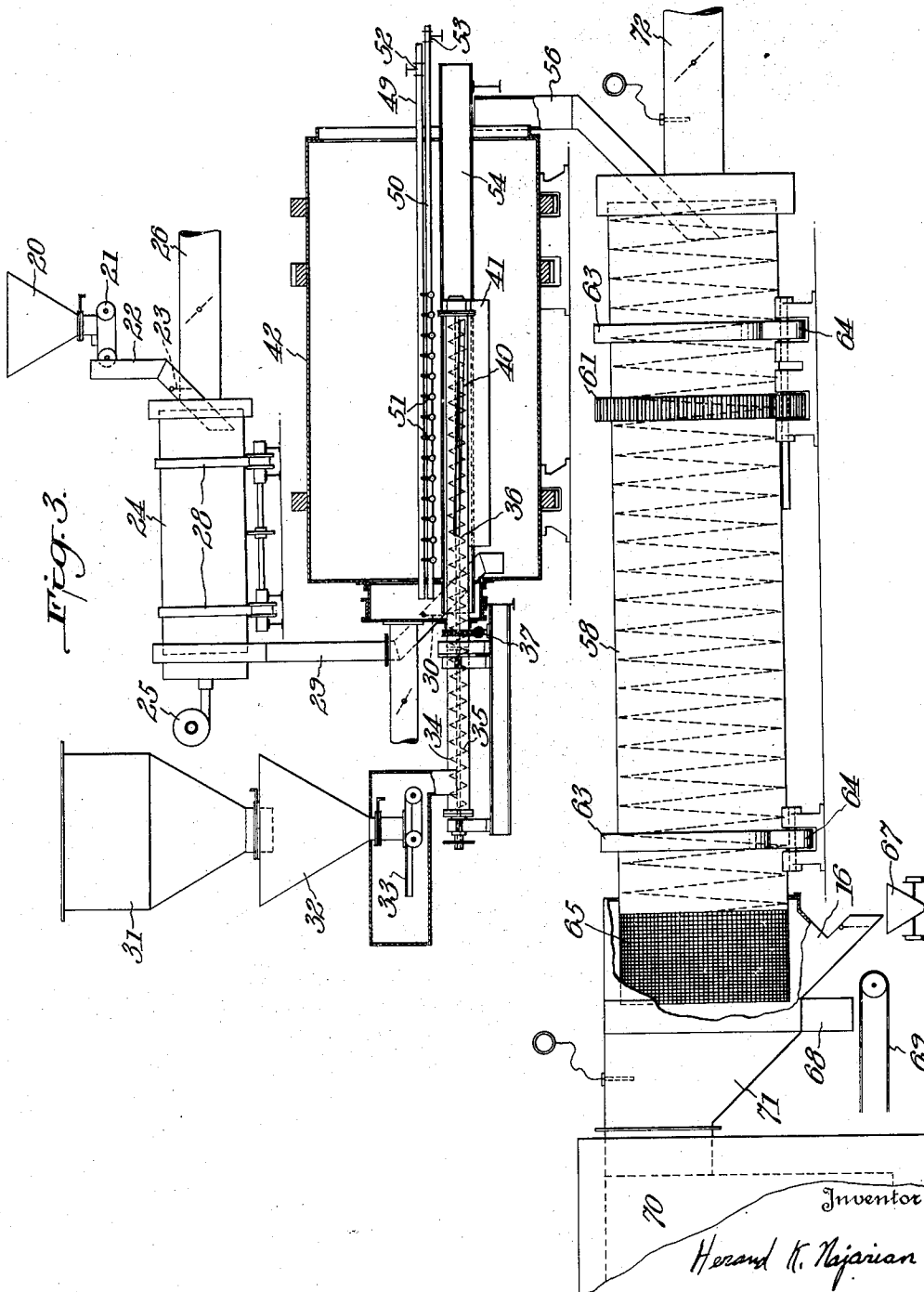
H. K. NAJARIAN

2,127,632

CONCRETIONARY AGGLOMERATE

Filed May 8, 1935

3 Sheets-Sheet 2



By

Inventor
Herand K. Najarian
Potter, Pierce + Scheffler

Attorneys.

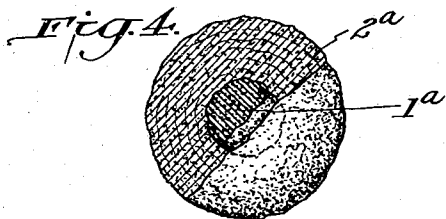
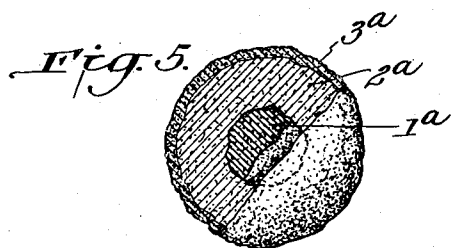
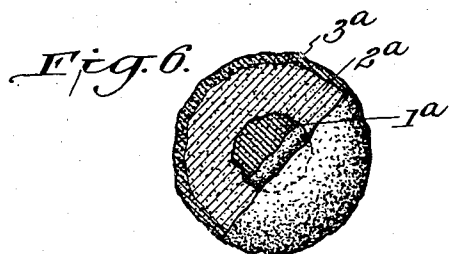
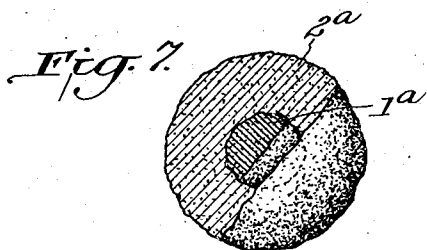
Aug. 23, 1938.

H. K. NAJARIAN
CONCRETIONARY AGGLOMERATE

2,127,632

Filed May 8, 1935

3 Sheets-Sheet 3



Inventor
Herold K. Najarian

By *Potter, Pierce & Sheffer*
Attorneys

UNITED STATES PATENT OFFICE

2,127,632

CONCRETIONARY AGGLOMERATE

Herand K. Najarian, Beaver, Pa., assignor to St. Joseph Lead Company, New York, N. Y., a corporation of New York

Application May 8, 1935, Serial No. 20,505

6 Claims. (Cl. 75—3)

This invention relates to carbonaceous and metalliferous concretionary bodies and to a method of making the same.

A principal object of the invention is the production of concretionary agglomerates useful in the industrial arts.

A further object of the invention is the production of metalliferous concretions useful in the smelting and reduction of ores and metallurgical products.

Another object of the invention is the production of carbonaceous agglomerates useful as industrial and domestic fuels.

A specific object of the invention is the production of zinciferous concretions useful in the smelting of zinc-bearing ores, industrial residues, and the like.

The solid concretionary bodies of the invention typically consist of a central core or nucleus, which is for certain purposes preferably a lump of carbonaceous material, such as coal or coke, coated with a multiplicity of layers of finely divided metalliferous material, or finely divided carbonaceous material, or both, together with binder, forming a dense shell about the nucleus. In the case of metalliferous concretions, carbonaceous material in either the finely divided state mixed with metalliferous material, or, used as a nucleus, may act as the reducing agent during a subsequent smelting operation. Where reducing agents are not required or are charged separately for certain manufacturing processes, such as the volatilization of PbO to produce a leaded zinc oxide, no reducing fuel will be used, the nucleus being, for example, zinc sinter or an inert substance. In the manufacture of lead sulphate ($PbSO_4$) the concretion is entirely made of galena (PbS) and an inert material for the matrix and nucleus. The binder, however, may be of sulphite liquor or suitable chemical substances. The principal purpose of the nucleus is to provide a surface on which is built up, in more or less concentric layers, metalliferous materials, carbonaceous materials, or a mixture of the two, together with such modifying agents as may be desirable, by alternate applications of a suitable binder and finely powdered metalliferous materials and/or finely powdered carbonaceous material, while a quantity of nuclei is being rolled unidirectionally in a suitable vessel, such as a rotating drum. The nuclei may consist, for example, of coke, coal, sintered ore, nodulized ore, pieces of ore of a character which may be subjected to sizing operation, or inert materials, such as limestone or brick.

A further purpose of the nuclei, which preferably should not have a great range of size, is to control the range of size of the ultimate concretionary bodies. Still another purpose of the nucleus is to immediately start the formation of

the concretion and to continue its formation at a uniform rate in its passage through the zone of manufacture within the drum. In addition to controlling within very close limits the ultimate size and variation in size of the concretionary body, the nucleus provides a solid core or center of definite weight, which in its unidirectional rolling within the drum will thoroughly compact the successive layers of the metalliferous materials as they are built up into one another, accelerating the wetting of the surfaces and the place alignment of each particle in such a manner that the whole outer shell is thoroughly compacted and requires a relatively small amount of plasticizing after passing from the zone of liquor and material application. The nucleus also serves in many cases to increase the strength of the resulting concretions.

By the process of the invention the nucleus is alternately coated with the agglomerating or binding composition and finely ground metalliferous or carbonaceous materials, and the whole is shaped or formed into a dense, spherical concretion, having each layer of the mass, as it is built up, individually consolidated upon itself and with the previously formed layer, the whole taking spherical form due to the condition of surface flow maintained by reason of the rolling contact imparted to the forming concretions by the rotation of the drum. Inasmuch as this rolling motion is continued until plasticizing, drying and reaction is practically complete, the product is a dense, hard, spherical concretion with a firmly coherent interior and a non-adherent, semi-polished surface, exhibiting in its dry state great resistance to crushing and adaptable either as the whole charge or as a suitable portion of the charge to blast and other shaft furnaces, vertical and horizontal retorts, electric and direct-fired furnaces, or any furnace suitable for the reduction or volatilization of metalliferous ores, or for use as an industrial or domestic fuel.

The method of manufacture of these concretionary bodies is characterized by its freedom from complications in either control or equipment, as will be apparent from the following description of the production of metalliferous concretions in accordance with the invention.

The metalliferous materials, which may consist of ores, sintered ores, waste oxides, drosses, furnace residues, flue dusts, metallic dusts, and waste or other materials of metalliferous content, are prepared by grinding, if necessary, together with a portion of their reduction fuel, in any suitable grinding apparatus, such as a ball mill, rod mill, or other comminuting device, to an appropriate fineness, preferably such that 40% or more will pass through a 200-mesh U. S. standard screen, the fineness of grinding being determined

by the natural properties of the metalliferous material with respect to its reactivity with the binder, surface adhesion, wettability and compacting qualities, it being desirable with some metalliferous materials to grind as much as 90% to -200 mesh U. S. standard screen.

The nucleus is prepared by screening to a predetermined size range, which, for the production of smelting concretions of say $\frac{3}{4}$ " diameter, should preferably be of such a size that they would pass a $\frac{1}{2}$ " screen and stay on a $\frac{1}{4}$ " screen. If concretions of larger size are desired, the size of the nuclei will be increased and the spread of the size between the "through" and "on" of the screens can be increased.

The binder should be applied in liquid form. Any binder suitable to the ores being formed into concretions and having the necessary binding properties either of itself or by chemical reaction with the constituents of the ores, can be used in this process. In this class are included carbonaceous, starch and cellulose products, the alkaline solutions, various metallic sulphate and chloride solutions, hydrocarbon products or mixtures thereof. As an example, for zinciferous ores a waste sulphite liquor may be utilized, preferably after diluting commercial sulphite liquor to 10° to 20° Baumé. The dilution will, in general, depend upon the initial temperature to which the nuclei are raised and the presence of any chemicals which may react, adding their heat to the residual heat of the nuclei. When the manufacture of ferrous concretions from blast furnace flue dust and the like is contemplated, calcium and magnesium chloride solutions, as well as various sulphate solutions, may be used advantageously. The chloride binders, in particular, are useful when treating copper ores or the waste products resulting from the smelting of copper. The quantity of binding liquor used in the manufacture of the concretions should be such that maximum strength and resistance to crushing are obtained in the finished concretions.

When using sulphite liquor as a binder, it is preferable that plasticizing be carried on to such an extent that the material surrounding the nuclei is in such a state that core or nucleus migration is imminent, but has not begun. If a batch of concretions is rotated in the forming drum, without the application of any heat, for too long a time, it will be found that the plasticity of the material has so developed that the core will have migrated near to the surface.

As a more particular example, when manufacturing concretions using a heated coke nucleus and finely ground (60% -200 mesh U. S. standard screen), zinciferous ores and waste products, with coke as a reducing fuel and sulphite liquor as a binder, (15° Baumé), after the concretions are built up to the desired size and the rotation and rolling in the drum continued for from 10 to 20 minutes after the application of liquor and metalliferous material has ceased, maximum strength will be developed in the dried concretion. This extra rolling or plasticizing process ensures a thoroughly wetted surface of each particle, which is in turn necessary to develop the maximum strength, as it produces a maximum distribution of the binding medium without migration of the nucleus. With certain ores and using chemical binders, such as those above mentioned, as well as various sulphate solutions, the heat of reaction may be of such magnitude and the hardening so rapid that neither this plasticizing nor subsequent drying will be necessary.

The invention will be more particularly described with reference to the accompanying drawings, in which:

Fig. 1 is an end elevation in partial section, and Fig. 2 is a side elevation in partial section, of an apparatus for the batch production of the concretionary bodies of the invention;

Fig. 3 is a partially diagrammatic layout of apparatus for the continuous production of the concretionary bodies of the invention; and

Figs. 4-7 are illustrative of some of the forms in which the concretionary bodies of the invention may be made.

Referring to Figs. 1 and 2, which are illustrative of the batch type of manufacturing, 1 is a drum of suitable dimensions mounted on one end of shaft 2, the drum having a central opening 3 opposite the shaft mounting. Through this opening screw conveyor 4 and a pipe 5 with suitable nozzles 10 project into the interior of the drum. Shaft 2 is carried on bearings 6 and is rotated through pulley 7, the shaft and drum rotating in the direction of arrow 8. A quantity of nucleus material, such as coke, sinter, limestone or the like in lump form is placed in the drum. Heat, if desirable, is applied to the material in the drum as, for instance, externally through burner 9.

As soon as the nucleus material is warmed, if desirable, to a temperature of 200 to 250° F., or other appropriate temperature, and while it is being rolled and tumbled over due to the rotation of the drum, the binder solution is sprayed on the nucleus material through pipe 5 and nozzles 10, which coats the individual particles of nucleus material with the liquid binder. Immediately screw conveyor 4 is started and finely pulverized metalliferous material, carboniferous material, or metalliferous material mixed with carbonaceous material, is fed from hopper 11 by means of screw conveyor 4 onto distributing apron 12, cascading off from apron 12 in a thin sheet onto the wetted rolling nucleus particles. The fine metalliferous and carbonaceous materials stick to the binder coating deposited by nozzles 10 on the nucleus material, forming a layer of metalliferous material on the nuclei, the particles of fine material being picked up and held together due to the adhesive properties of the binder.

As the drum rotates, each nucleus with its accumulating metalliferous coating alternately passes through the spray of binder and fine metalliferous material, continually getting larger in diameter and resulting in a spherical body in the form of a concretion built on a solid core, as shown in partial section in Fig. 4, for example.

The shell portion, or that portion external to the nucleus of the concretionary body, is thoroughly compacted by the rolling, folding over, and tumbling action in the drum, the motion being continuous and unidirectional.

The preferable peripheral speed of a drum 8 feet in diameter is 90 feet per minute. It is preferable to have the drum subject to variable speed control with a range of from 65 to 100 feet peripheral speed per minute, in order that until the operation is well established that speed may be varied to attain at all times uniform consistency and compacting qualities of the concretions. The time required under otherwise constant conditions will depend upon the ultimate size of the concretion desired, but generally the application of the liquor and metalliferous material is such that when using a $\frac{1}{2}$ " to

— $\frac{3}{4}$ " nucleus, a concretion approximately 1 to $1\frac{1}{8}$ " in diameter is built up in 20 minutes. The resulting spherical-shaped concretion will contain about 6 to 10% moisture, depending upon the initial moisture and temperature of the nucleus, the exothermic heat from chemical reaction, the fineness of the metalliferous material at introduction, and the type of binder used.

When the desired predeterminate size of the concretions has been reached, the flow of liquor and of metalliferous material is stopped and, in the case of concretions manufactured with sulphite liquor as a binder, the drum continues to operate for from 10 to 20 minutes to thoroughly plasticize and compact the metalliferous materials surrounding the nuclei, at which time the drying will be started. Drying may be accomplished by the gradual application of heat either directly or indirectly in the manufacturing drum, or the concretion may be discharged from the drum through gate 13 into separate drying apparatus such as a rotary drum, wherein their temperature will be gradually raised during a period of from 30 to 90 minutes, from a temperature of 120° F. to 200° F., with an additional period of approximately 30 to 60 minutes after discharge from this drying apparatus for further hardening before subjecting the concretions to severe handling conditions. This method of drying is especially advantageous when sulphite liquor is used as a binder for zinciferous materials.

The concretions are now ready for shipment or use, for example, for charging into the smelting furnace, retort, blast furnace, or other type of furnace.

Fig. 3 illustrates a method for the continuous manufacture of carboniferous or metalliferous concretions.

Referring to Fig. 3, and describing by way of example the preparation of zinciferous concretions with coke as a nucleus, the coke is stored in bin 20, from which it is proportioned in the correct amount by constant weight feeder 21 into chute 22 and thence into drum 24, which is rotatable about its axis on tires 28. For the purpose of preheating the coke, gas burner 25 is located at the discharge end of drum 24, the passage of the hot gas through this drum and to exit 26 heating the coke. Chute 22 has a check gate 23 in order to prevent the flow of gases upwardly through the chute. Drum 24 discharges heated coke continuously into chute 29, which carries the coke nuclei into drum 42. Chute 29 also has a check gate 30.

The zinciferous materials are stored in bin 31, which discharges into auxiliary bin 32, in order to prevent the flooding of constant weight feeder 33 which feeds the material from auxiliary bin 32 into screw conveyor 34. Casing 36 is a continuation of screw conveyor casing 35, but is rotatable about its axis by means of worm wheel 37. Rotatable casing 36 has a longitudinal slot 40, through which the feed of zinciferous material is discharged in a more or less constant stream onto cascade pan 41, from which it flows in a thin, relatively even sheet, onto the nuclei in the drum.

Simultaneously with the beginning of discharge of the zinciferous materials from slot 40 onto cascade pan 41, the flow of binder liquid is started from spray nozzles 51, the binder liquid being supplied, in the preferred method, through pipe 50 and controlled by valve 53. Compressed air at a low pressure is supplied through pipe 49, controlled by valve 52, and is independently

pipled to each spray nozzle 51. Other types of spray nozzles may be used, but the air atomizing type is preferable, inasmuch as it provides a very fine, thin spray which builds up the concretions in very thin regular layers, contributing to the ultimate strength of the concretions due to the fact that the rolling action is more effective in consolidating the particles when thin layers of the binder and metalliferous material are applied than it is when thick layers are applied. Screw conveyor 34 and casing 36 which is rotatable to control the distribution of flow from slot 40 are supported by structural member 54.

After the concretions are well formed they pass into the lower end of the drum which operates as a plasticizing chamber, no liquid or metalliferous material being further applied to the concretions. The rolling action in this section of the drum ensures a thorough wetting and consolidation of all particles.

The concretions are discharged from drum 42 into chute 56 and thence into dryer 58, which is rotatable about its axis by gear 61. The drum rotates on tires 63 and rollers 64.

The concretions in passing through drum 58 meet with a countercurrent of hot gases from furnace 70 through breaching 71, which ultimately discharges through waste gas exit 72. At the discharge end of dryer 58 a screen 65 is fixed, which discharges the fines which have come through the system into boot 16 and through its check gate into car or other suitable conveying equipment 67, whereby the fines are again discharged to the grinding system for incorporation into the original charge. The concretions which stay on the screen 65 are discharged by means of boot 68 and through its check gate onto conveyor 69, thence to the smelting furnaces or storage.

When using inert nuclei, heater 24 may in most cases be dispensed with and the nuclei may be fed directly from the feeder 21 into chute 29. Heating of the nuclei is, however, preferable as the residual heat will prevent a large absorption of moisture by the nuclei, which must be driven off during subsequent drying. Any considerable absorption of moisture by the nuclei slows the drying period and renders the destruction of the concretions possible through the aggregation of too great an internal pressure by steam generated during rapid drying. When using chemical binders with rapid reaction, dryer 58 may be dispensed with and the concretions discharged directly from chute 56 onto conveyor 69.

It will be observed from Fig. 3 that the concretions are subject from the time of the entrance of the nuclei into drum 42 to a constant rolling action tending to form them into spheres with a constant increase in size until the application of the metalliferous material and binding liquid ceases, after which the size does not appreciably change. Such change as there is appears to be in the direction of a slight reduction in diameter due to the constant working and rolling in the plasticizing or discharge end of the drum. Drum 24 and furnace 70 may be fired with any kind of gaseous, liquid, solid fuels.

Fig. 4 represents one type of concretion made by the method of the invention, in which the nucleus 1a may be a piece of inert material, such as fire brick or other waste inert materials, or it may be of more active material, such as coke, coal, or the like. The portion 2a external to the nucleus may be of finely ground ores, sinter, residues, oxides, flue dusts, drosses, or other mate-

rials requiring carbon for their reduction, advantageously mixed with finely ground coke or other carbonaceous material in sufficient quantity to reduce the metalliferous oxides to the metallic state. Finely divided metals may also be added to the mix and efficiently retreated by the process. Modifying and reacting ingredients of various kinds may be added to the mix.

In the case of carbonaceous concretions for use as fuel the nucleus 1a, advantageously consists of coke, coal, or other solid combustible, while the shell 2a is built up of finely pulverized coal, coke, semi-coke and the like materials. Suitable binders for these materials are sulphite liquor, crude oil, tars, asphalt residuum, emulsions and the like. The advantages of the invention in the preparation of fuels are particularly striking in the following cases:

(1) Agglomeration of anthracite culm, preferably after cleaning by flotation to reduce slate and other impurities, the product being a concretionary fuel of any desired size, preferably corresponding to various sizes of anthracite coal marketed, such as nut, egg, etc. These will, of course, be more or less spherical in form. A baking or low temperature coking will improve the product by driving off easily volatilized constituents of the binder and making the produce smokeless and very similar in character to anthracite domestic coal.

(2) Manufacture of concretionary fuel aggregates from coke fines, which do not find a ready market as fuel.

(3) Manufacture of so-called smokeless fuel aggregates from high volatile, free-flowing, bituminous coals. Such coals soften in furnaces and burn with considerable smoke and soot, resulting in incomplete and consequently inefficient burning of fuel. By subjecting such high volatile coals to low temperature coking, recovering the valuable gas and tar products, grinding the resulting semi-coke, and agglomerating the fine product by the method of the invention to produce concretionary aggregates, a readily combustible, dense, smokeless fuel ideally suited for burning in domestic furnaces, stokers, etc., and for making coal gas or water gas, is produced.

Fig. 5 shows a modification where the character of the metalliferous material is such that it produces corrosive substances or reactive slags during the smelting. In such cases the concretion can be given a further outer coating 3a of refractory material, such as clay, coke, coal, or mixtures to prevent the ore from coming into contact with the retort or furnace walls, thereby obviating the corrosive action. It will be apparent that these additional materials may be applied in exactly the same way as the metalliferous coating was applied to the nucleus, as described above.

Similarly, a shell 3a of chloride salts or the like may be applied, as shown in Fig. 6. It is believed that such salts act as a filter for the volatile metal fumes and are useful in preventing the formation of "blue billy" in zinc smelting retorts and furnaces, and a reduction in the formation of blue powder in the condensers.

The concretionary fuel aggregates described above may likewise be given a coating, for example, of a mixture of powdered fuel and asphalt for the purpose of increasing their resistance to moisture.

The above mentioned salts may be made a part of the concretion shown in Fig. 4 by mixing the salt with the metalliferous materials, or dissolv-

ing the salts in the liquid binder, with beneficial results.

Fig. 7 illustrates a concretion with a zinciferous agglomerate as nucleus 1a. This agglomerate may be sinter, residue, slag or the like, whose zinc content is still relatively high, or it may be high-grade sinter. The portion 2a of the concretion external to the nucleus may be wholly made up of the carbonaceous reduction fuel held with a suitable binder and will have advantages in preventing the lower grade sinters and residues rendering the operation difficult due to the slagging characteristics of the nucleus.

Following are several examples of formulas for metalliferous concretions, which particularly apply to zinciferous, ferriferous and plumbiferous materials. It is to be understood that these examples are illustrative of the process only, as it will readily be recognized that the concretions and the method of manufacturing the same are applicable generally in the metallurgical field, both ferrous and non-ferrous.

Example No. 1

Material	Size	Composition	Weight
		Percent	Pounds
Roasted zinc ore.....	99% -100 M.	Zn 69.00 Pb .05 Fe 7.00 S .30	900
Coke, ground with ore (reclaim).	91% -200 M.	Zn 7.00 Fe 5.00 S .10	100
Coke nuclei.....	+3/8"-3/4"	Fe 5.00 S .10	80
Sulphite liquor, 10° Baumé.....			185

Example No. 2

Material	Composition	Weight
	Percent	Pounds
Dross.....	Zn 65.00 Other metals 27.00	120
Drop ZnO.....	Zn 72.00 Other metals 21.00	317
Magnetic zinc residue.....	Zn 27.20 SiO ₂ 23.40 Fe 18.70 C 7.20	413
Coke ground with ore.....		150
Sinter nuclei.....	Zn 59.80 Fe 7.90	210
Sulphite liquor, 10° Baumé.....		185

Example No. 3

Material	Composition	Weight
	Percent	Pounds
Drop zinc oxide.....	Zn 72.00 Other metals 21.00 C 2.00	280
Magnetic zinc residue.....	Zn 27.20 Other metals 4.00 SiO ₂ 23.40 Fe 18.70 C 7.20	615
Reclaim coke ground with ore.....	Zn 7.00 Fe 4.00	110
Lime rock ground with ore.....		30
Coke nuclei.....	Fe 3.00 S .85	70
Sulphite liquor, 10° Baumé.....		185

The above Examples 1-3 are useful in the man-

ufacture of lead-free zinc oxides, zinc metals, and other zinc products.

Examples 4, 5 and 6 are used in the manufacture of leaded zinc oxide and relatively high lead zinc metal.

Example No. 4

Material	Composition	Weight
	Percent	Pounds
Flue dust.....	Zn 54.00 Pb 15.10 Fe 7.00 S 1.10	890
Reclaimed coke.....	Zn 7.00	110
Coke nuclei.....		70
Sulphite liquor, 10° B _e		185

Example No. 5

Material	Composition	Weight
	Percent	Pounds
Flue dust.....	Zn 54.00 Pb 15.10 Fe 7.00 S 1.10	890
Reclaimed coke.....	Zn 7.00	190
Sinter nuclei.....	Zn 59.80 Metallics 9.40 SiO ₂ 8.80 Fe 7.90 S .10	210
Sulphite liquor, 10° B _e		185

Example No. 6

Material	Composition	Weight
	Percent	Pounds
Flue dust.....	Zn 54.00 Pb 15.10 Fe 7.00 S 1.10	1,000
Sinter nuclei.....	Zn 59.80 Metallics 9.40 SiO ₂ 8.80 Fe 7.90 S .10	210
Sulphite liquor, 10° B _e		165

In Example 7 is a mix which may be used in the manufacture of basic lead sulphate.

Example No. 7

Material	Composition	Weight
	Percent	Pounds
Galena—PbS.....	Pb 78.00 Fe 1.00 S 12.00	900
Reclaimed coke.....	Zn 7.00	70
Sulphur.....		30
Coke nuclei (reclaim coke).....	Zn 7.00	70
Sulphite liquor, 10° B _e		160

The following is a typical example of the manufacture of the concretions for iron blast furnace practice, using blast furnace flue dust.

Example No. 8

Material	Composition	Weight
	Percent	Pounds
Iron blast furnace flue dust.....	Fe 44.00 C 14.00	940
Coke nuclei.....		60
Liquor (ferrous sulphate solution .4% dry FeSO ₄).....		120

It is obvious from the above examples that a

wide variety of metalliferous materials not mentioned may be incorporated into the concretions. Also that these charges may be made up in such a way that they are self-fluxing, for instance, for blast furnace practice, the ferrous materials, lime, silica and any other desirable fluxing materials for slag control may be directly incorporated into the concretion, and that the ratio of nuclei to pulverulent material may be widely varied to suit any particular smelting necessity.

Careful consideration of the manufacturing process, structure of the material, and high strength of the finished concretion (a 1" spherical concretion after drying having a crushing strength in excess of 500 pounds) will make apparent its adaptability for a wide range of metallurgical processes. Several of its advantages may be pointed out; for instance, the very small excess of reduction fuel required over the theoretical amount. In the case of reducing zinc, for example, where it is customary to use from 35 to 40 percent carbonaceous fuel, based on the zinc charge, the concretions of this invention require only from 15 to 30 percent, depending upon the zinc content of the materials under treatment. In spite of the low carbon content of the concretions, the time and temperature necessary to complete reduction are materially reduced. For example, in the ordinary Belgian type zinc retort, reduction of the zinc-bearing concretions will be complete in from 6 to 8 hours at a temperature of 1200° C., contrasted with a time of from 16 to 18 hours when smelting the ordinary loose charge which is commonly used.

Furthermore, due to the intimate mixture of the carbonaceous and zinciferous materials, the temperature at which reduction reactions have comparable efficiencies would be 975° C. for the concretions and 1225° C. for the loose charges of ordinary practice. This is due to the fact that in the reduction of an aggregate, such as a lump of ore, sinter, or an agglomerate of ore alone, the reduction progresses from the outside surface inwardly, the difficulties of bringing about contact with the carbonaceous material, or of effecting carbonaceous gas penetration being greatly increased as the size of the particle increases, inasmuch as the inert materials carried by the ore when it is in the form of lumps or agglomerates having appreciable size, serve to segregate as reduction proceeds on the surface of the particles, preventing free carbon contact and making the penetration of the carbonaceous gases difficult. Therefore, the time and temperature required for the final efficient reduction of such ores are greatly increased over that required by the finely ground metalliferous materials intimately mixed with finely ground carbonaceous materials in the concretions of this invention.

With a carbonaceous nucleus, considerable vapor pressure at the temperature of reduction must be exerted from that direction and reduction proceeds rapidly, inasmuch as the novel conditions of structure of the concretion promote the realization of nearly ideal reduction.

The concretions being spherical, or nearly so, in form, the space between the bodies for the circulation of the gases and vapors is at a maximum, thus resulting in a very rapid heat transfer from one part of the retort to the other and the assurance, due to the open charge, that local pressures will not be built up, which seriously impair smelting efficiency. Inasmuch as, referring particularly to zinciferous ores, the prefer-

able carbonaceous content is metallurgical coke containing relatively low sulphur and very low residual volatile content, the concretions of the invention may be used in the direct production of the metallic oxides from the volatile metals, and a high grade product obtained, which cannot be realized, particularly in the manufacture of zinc oxides or the basic lead sulphates by the fuming process, when the raw zinciferous or plumbiferous materials are briquetted with the coking bituminous coals. Inasmuch as the limitations placed upon the coking process by the reduction temperature of these metalliferous materials are such that the volatile content of the briquette or agglomerate cannot be reduced below about 2%, the result is that as this material is subsequently reduced in the smelting furnace, the remaining volatile hydrocarbon of the briquette or agglomerate is distilled off in the reduction process and carried out with the gases and vapors, excessively discoloring the oxides produced by these processes and making them unfit for commercial use in many of the arts. Furthermore, a briquette made without the aid of the flowing or coking coals, or an excessive amount of tar or pitch, has not proved satisfactory in shaft furnaces, due largely to the fact that, although great pressures are used by the numerous briquette pressing devices, the moisture content at the time of pressing must be kept relatively low, with the result that the particles are not thoroughly wetted, that the binder and the matrix formed by the subsequent reaction due to heat or chemical reaction is poorly distributed, and that when the briquette is highly heated it sands rapidly, causing a loss of furnace porosity and a consequent loss of smelting efficiency due to the difficulties of obtaining uniform heat penetration to all parts of the charge.

In blast furnace smelting, if the charge consists of concretionary agglomerates, made by using the fuel portion of the charge in the form of lumps of coke, coal, or charcoal as nuclei, and coating them with the finely ground mixture of ores, fluxes, flue dust and the like, improved operation and reduction in fuel consumption are obtained due to the fact that the concretions permit free and more uniform circulation of reducing gases in the furnace while the coating on the fuel inhibits the dissolution of the carbon in the fuel at the upper zones of the blast furnace by ascending carbonic acid gas.

The solid nucleus of the concretion of this invention—whatever it may be composed of—

greatly reinforces the structure and prevents breakage and crumbling.

The production costs of the metalliferous concretions are substantially less than sintering, briquetting, and other well known agglomerating processes on high grade ores, and when low grade products or residues are to be treated, these economies are greatly increased over the processes generally practiced in the arts. The concretions form an ideal charge either by themselves or in combination with other metalliferous charge, such as sinter, ore, or other agglomerated materials in resistance type electric furnaces, and particularly in those furnaces in which the charge is the resistor, horizontal or vertical retorts, or in blast furnaces, reverberatory furnaces, or combination retort and electric resistance furnaces.

I claim:

1. A method of making concretionary aggregates which comprises contacting solid particles alternately with finely divided solid material and a binder material while subjecting the particles to continuous rolling.

2. A method of making concretionary aggregates which comprises contacting solid particles with finely divided solid material and a binder material while subjecting the particles to continuous rolling until a shell of desired size has built up about the solid particles, and thereafter continuing the rolling operation until the substance of said shell is well plasticized.

3. A method of making concretionary aggregates which comprises contacting solid particles with finely divided solid material and a binder material while subjecting the particles to continuous rolling until a shell of desired size has built up about the solid particles, thereafter continuing the rolling operation until the substance of said shell is well plasticized, and indurating the aggregates thus formed by heating.

4. Concretionary aggregates comprising a solid carbonaceous nuclear particle and a surrounding shell of indurated, finely divided solid metalliferous material and binder material.

5. Concretionary aggregates comprising a solid nuclear particle, a surrounding shell of indurated, finely divided solid metalliferous material and binder material, and an external coating of finely divided refractory material.

6. Zinciferous concretions comprising a solid nuclear particle of coke and a surrounding shell of indurated zinciferous material and binder material.

HERAND K. NAJARIAN.