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## METHOD OF FORMING METALLURGICAL BRIQUETTES OF ZINCIFEROUS MATERIAL

Roland G. Crane, Sewaren, N. J., and Othon J. Cerna, Nueva Rosita, San Juan de Sabinas, Mexico, assignors to American Smelting and Refining Company, New York, N. Y., a corporation of New Jersey

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This invention relates to improved metallurgical briquettes of zinciferous material, their preparation and use. More particularly, it relates to metallurgical briquettes employing oil and clay as a binder, which briquettes are particularly useful for smelting in a vertical retort.

In the vertical retort process for smelting zinc-bearing materials, it is the commercial practice to form oxidic zinc-containing material into metallurgical briquettes composed of an intimate mixture of the zinc-bearing material and a high grade coking quality coal as a reducing agent. The briquettes are smelted by passing them downwardly in a vertical column through a vertical retort. During their passage through the retort, the zinc values in the briquettes are reduced to metallic zinc which is released from the briquettes as a vapor which is then condensed and recovered in an appropriate condenser. The dezincized residues from the smelting may then be further processed to recover remaining metal values therein, especially the lead and the precious metal values.

The material to be formed into briquettes is prepared in a procedure known in the art as "chasing", in which ground particles of the zinciferous material, the coal and waste liquor from the sulfite treatment of cellulose material as a binder are intimately mixed together. The mixing is performed in a device well known in the art under various names, such as a chaser or Chilean mill wherein the materials are subjected to the pressure of a heavy bearing load while being mixed and kneaded to obtain a semi-plastic mass for the subsequent briquetting operation which is usually performed by roll-pressing in one or more steps. Thereafter, the briquettes are coked prior to being smelted in the vertical retort.

It is necessary, especially in the vertical retort process, that the briquettes be capable of withstanding the deforming and shattering forces to which they are subjected in smelting without forming an undue amount of powder or small fragments known in the art as "fines." Thus, in passing through the vertical retort the briquettes are subjected to abrasion and to the shattering force of the weight of the entire column of briquettes in the retort. The ability of the briquettes to withstand these forces during the retorting is measured by their so-called "residual strength." Although the process can tolerate the presence of some fines, the efficiency of the process is adversely affected to the extent that fines occur. Also, the formation of an unduly large amount of fines during the smelting of the briquettes may render the process inoperative due to plugging. While it is not possible to eliminate the formation of fines entirely, methods and means are constantly sought by the art whereby the formation of fines may be reduced to a minimum consistent with an economical operation.

Although not as important as residue strength, it is nevertheless important that the briquettes possess a strength in the uncoked and in the coked states which is as high as possible. The strength of the briquettes in these two states is known in the art as the "green strength" and "coked strength" respectively. Thus, it is desirable

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that the green strength be as high as possible in order that the briquettes may withstand the necessary handling to which they are subjected with a minimum amount of deformation and formation of fines. This is true also of the coked briquettes. Moreover, it is also highly desirable that a minimum amount of fines be formed during the coking operation.

Heretofore, for want of a better procedure, it has been considered necessary in commercial practice to use a high grade bituminous coking coal of a type comparable to that found in the vicinity of Connellsville, Pennsylvania, in making the briquettes.

One of the advantages of the present invention is that it provides a metallurgical briquette having improved residual strength, as well as improved coked strength and satisfactory green strength. Another advantage is found in the use of novel and inexpensive binder materials to obtain these results. A further and extremely important advantage resides in the fact that lower grade bituminous coking coal may be used in preparing metallurgical briquettes of zinciferous material suitable for vertical retort smelting. Thus, by practice of the invention, the art is no longer restricted to the use of a high grade coking coal and now may employ cheaper or more readily available types of coal which were heretofore considered to be unusable in preparing briquettes for smelting in a vertical retort.

The invention broadly comprehends a green metallurgical briquette comprised of an intimate mixture of a zinciferous material containing oxidic zinc values reducible to metallic zinc, bituminous coking coal, a plastic kaolinitic-base clay having a softening point in excess of about 2000° F. and a mineral oil having a viscosity of about 200–1000 seconds, Saybold-Fural, at 122° F. To obtain best results as to residual strength in the final dezincized briquettes, the green briquettes are comprised approximately by weight of about 15–40% of the coal, 0–25% of a diluent material, 2–7% water, 1–6% of the clay, 2–7% of the mineral oil, and the remainder an oxidic zinc-containing material. The green briquettes may be formed into any convenient size; however, those having an approximate dimension of about 4" in length and 2–3" in width and breadth are generally preferred.

The invention may be practiced in connection with any zinc-bearing material containing zinc in a form which may be reduced to metallic zinc, or which has been converted to such a reducible form; that is to say, the zinc is in a form that may be considered to be an oxide. Thus, for example, zinc oxide, zinc silicate, zinc ferrite, or zinc aluminate ores and the like may be used. Zinc sulfate and zinc sulfide ores may also be used after they have been roasted or otherwise treated to convert the zinc to the zinc oxide form. In general, it is preferred to use a ground sinter obtained, for example, by roasting, sintering and grinding a sulfidic zinc concentrate; on zinc fume such as that obtained from zincy lead blast furnace slags by the so-called fuming process; or mixtures of sinter and fume.

A bituminous coking coal of any quality may be used as the reducing agent in combination with the present binder materials to obtain enhanced residual strength in the briquettes or to obtain improvements in the physical characteristics which would not otherwise be obtained except by the use of the present oil and clay binder materials. Thus, a high grade coking coal such as the type found in the vicinity of Connellsville, Pa., or any other bituminous coking coal may be used, depending upon its cheapness and availability to the site of the smelting plant. Bituminous coking coal typical of that found in Colorado, Australia and Mexico, has been found to give excellent results in preparing briquettes suitable for use in smelting in vertical retorts. It will be noted

that the present bituminous coking coal is distinguishable in the art from coal which is known therein as sub-bituminous coal.

It likewise will be understood that the bituminous coking coal also possesses capacity as a binder. Such capacity, however, is not sufficient in itself to produce briquettes of operative strength and must be supplemented or enhanced to obtain briquettes which are satisfactory in this respect. It has been found that the binding capacity of the bituminous coal varies depending upon the particular coal used and its source; and that as the binding capacity decreases the optimum amount of such coal in the green briquettes increases.

For best residual strength, the green briquettes should contain about 15-40% by weight of the bituminous coking coal. Moreover, amounts of 15% by weight or more are desirable to insure the presence of sufficient reducing material in the briquettes, especially when the preferred amounts of reducible values are present therein. In addition, amounts in excess of about 40% by weight of such coal are undesirable for economic reasons. Within this range, the optimum amount or the optimum economic amount of the bituminous coal will vary, depending upon its binding capacity; and the amount actually used may be varied accordingly, if desired. When less than about 40% of such coal is used in the green briquettes, an appropriate diluent material may be substituted for the thus replaced coal. In general, it is preferred that the green briquettes contain about 15-30% by weight of the bituminous coal and 10-20% by weight of diluent material.

The diluent material should be a solid material which normally retains its solid state at the coking and smelting temperatures employed and which does not adversely affect the physical characteristics of the briquettes. Thus a solid carbonaceous material having a low volatile matter content, for example ground coke or anthracite coal, is used as the diluent material. Of these preferred examples, coke is the most preferred.

Plastic kaolinitic-base clays having a softening point in excess of about 2000° F. such as ball clays, plastic kaolins or plastic fire clays are preferred in amounts of about 1-6% by weight of the green briquettes. A fire clay having a softening point at least in excess of about 2200° F., in amounts constituting at least about 2.5% of the green briquette weight, is most preferred. It has been found that little or no enhancement of the residual strength of the briquettes is obtained with bentonite clay, this being a clay of the Montmorillonite type. It should be understood, however, that clays of this type and other materials may be present or added to the briquettes, if desired, to the extent that they do not injure or reduce the physical characteristics of the briquettes.

The mineral oil may be a crude petroleum or residual oil or other non-polar or similar non-water soluble mineral oil having a viscosity of about 200-1000 sec. at 122° F. as measured by the Saybold-Fural method and apparatus. This range of viscosity corresponds to a specific gravity in the range of about 10-16° A. P. I. gravity. Crude or residual oils having a viscosity in this range may be used, per se, or heavier oils inside or outside the range may be blended with distillate oils or lighter fractions to obtain a mixed oil of desired viscosity within the range. It has been found that mineral oils having a viscosity above about 1000 sec. at 122° F., Saybold-Fural, are too viscous to be used effectively. It has also been found that as the viscosity of an oil decreases, its effectiveness also decreases; and that an oil having a viscosity below about 200 sec. at 122° F., Saybold-Fural, is not sufficiently effective for use in the briquettes.

It is not necessary that water be present in the green briquettes to obtain enhancement of the residual strength of the dezinced briquettes. To obtain best results as to green strength when no water is used, it is desirable to

employ higher amounts of oil, preferably in excess of about 5% and usually in amounts of about 6-7% by weight of the green briquettes, although oil above or below these amounts may also be used if desired. However, the presence of water in the green briquettes is both desirable and preferred as it enhances the plasticity of the mixture to be briquetted as well as the green strength of the resulting briquettes.

It has been found that the amount of water to be used is largely dependent upon the amount of oil used. When both these ingredients are present, amounts in the range of about 2 to about 7% by weight of each of them, based upon the green weight of the briquettes, are preferred for best results as to residual strength. For high green strength as well as high strength during coking, the oil is present preferably in amounts not exceeding about 5% and the water in amounts not exceeding about 4%, by weight of the green briquettes. For highest green strength, about 2-5% of the oil and 2-4% of the water are used. Water, when used, may be added as such or carried as moisture content into the green briquettes by one or more of the solid ingredients. To develop optimum plasticity in the mixture to be briquetted, it is preferred that the moisture of such solids be sufficiently low so as to require the addition of physical water to obtain the desired amount of total water in the green briquettes.

The particle size of the solid materials affects the maximum physical properties developed by the briquettes. The various solid ingredients are preferably in a relatively finely divided state and, where necessary, they are reduced to this state by grinding. In general, it has been found that as the degree of subdivision of the solid material is increased, higher maximum values of the physical properties are developed in the briquettes. For best results, substantially all the bituminous coal and the zinc-bearing material should be ground so as to pass through a 14-mesh screen and at least 15% of each of them through a 200-mesh screen, while substantially all of the diluent material should be ground to pass through a ¼" screen and at least 10% through a 200-mesh screen. Where the clay occurs in lumps or relatively large aggregates, these should be reduced to masses about ¼" in size. It has been found that grinding of the clay has no apparent effect upon the physical properties of the briquettes due, it is believed, to the fact that the naturally occurring particles of which the lump or aggregate is comprised are already in a highly divided state. As used herein both in the specification and the claims, a standard screen refers to a standard Tyler screen.

The ingredients used in preparing the green briquettes are intimately mixed together by the "chasing" procedure referred to earlier, to obtain a semi-plastic mass for briquetting. With the present binder material it has been found that plasticity and physical characteristics are improved as the chasing time is increased. It has also been found that for best results the total chasing time should not be less than about 10 minutes. Although the mixture may be chased for a period in excess of about 10 minutes up to as much as 60 minutes or more, the slight increase in physical properties of the briquettes for periods in excess of about 10 minutes does not generally warrant the added expense. All of the ingredients may be added at the beginning of the chasing period or, if desired, the oil, clay or water may be added during the chasing period. With the latter procedure, it is desirable that all of the oil and clay be in the mixture at least during the latter half of the chasing period. The zinciferous material may be, and preferably is, preliminarily mixed with the coal and the diluent prior to the chasing. The semi-plastic mixture resulting from the chasing may then be formed into briquettes of appropriate size in any suitable briquetting machine. The briquetting may be performed by extrusion or roll-press-

ing, in one or more steps; roll-pressing in two steps being preferred.

If water has been used to prepare the green briquettes, they may be given a preliminary drying at temperatures below about 400° F., preferably below about 200° F., prior to being coked; or if desired, the green briquettes may be passed directly to the coker. The coking preferably is conducted at temperatures of about 1000–1800° F.; coking temperatures above about 1800° F. being avoided in order to avoid an undue loss of zinc values during the coking step. While being heated to the coking temperature, the briquettes pass through a relatively soft stage at temperatures in the range of about 400–750° F. During this stage, they are relatively prone to the formation of fines, especially in coking apparatus of the type in which there is relative motion between the briquettes in the coking bed. To assist in the reduction of fines during the coking operation, the outer surface of the individual briquettes is formed into a coked or "case-hardened" shell as rapidly as possible. This is accomplished in the coking operation by subjecting the briquettes initially to a temperature of at least 800° F. The coking, including the case-hardening step, is preferably conducted with radiant heat and the thickness of the bed of briquettes, especially during the case-hardening, is controlled to permit a sufficiently rapid formation of the coked shell on the briquettes on and adjacent to the bottom of the bed. Preferably also, a bed depth below about 8–9 inches is used during the "case-hardening" in the initial heating, and such depth is preferably also maintained during the rest of the coking. Any fines produced during or after the coking, or any fines from the green briquettes, may be and preferably are returned for use in preparing the green briquettes. Such fines are ground where necessary and mixed with the zinciferous material, the diluent material and the bituminous coal prior to the chassing.

Although the coked briquettes of the invention may be retorted in a horizontal retort, the invention is particularly useful in connection with vertical retort smelting because of the enhanced residual strength obtainable in the briquettes. Any type of vertical retort may be used. For example, the retort may be a suitably mounted vertical silicon-carbide retort heated by fuel firing, or an electrical resistance type retort furnace.

The invention is further illustrated in the following examples. It should be understood, however, that the examples are given for purposes of illustration and the invention in its broader aspects is not limited thereto.

#### EXAMPLES

Green briquettes were prepared having the composition indicated in the tabulation of the examples in Table I. The sinter was a zinciferous material containing 63.1% of reducible oxidic zinc and was prepared by roasting zinc sulfide concentrate and then grinding the roasted sinter. The coal was a washed and ground bituminous coking coal found in the state of Coahuila, Mexico, in the vicinity of the city of Rosita which by analysis showed the following typical composition: 25% volatile matter, 60% fixed carbon, 15% ash. The sinter and the coal were separately ground so that substantially all of each of them passed through a 14-mesh screen and at least 15% of each of them passed through a 200-mesh screen. The coke was ground coke obtained by coking the Rosita coal and contained 5% volatile matter, 70% fixed carbon and 25% ash. The coke was ground so that substantially all of it passed through a ¼" screen and at least 10% through a 10-mesh screen. The fire clay was a #1 grade fire clay found in the vicinity of Goss, Missouri. These plastic clays have a softening point of about 3100–3200° F. as measured by the Seger Cone test. The bentonite clay was a Bentonango bentonite clay. The crude oil was a so-called "Ebano" crude found in the State of Tamaulipas, Mexico.

It had a specific gravity of 0.9821 at 20° C., a flash point of 39° C. and a viscosity of 515 seconds at 122° F., Saybold-Fural. The fuel oil was a residual type oil having a specific gravity of 0.9635 at 20° C., a flash point of 115° C. and a viscosity of 351 seconds at 122° F., Saybold Fural.

The green mixture for briquetting was prepared by chassing the sinter, coal, coke and clay together in the dry state for one minute. The water was then added and the wet mixture was chassed for four minutes. Thereafter, the oil which was at a temperature of 50° C. was added and the resulting mixture further chassed for a period of five minutes. The green mixture was then formed into briquettes of about 4 inches in length and 2–3 inches in width and breadth by roll-pressing in two passes, i. e. by passing the mixture through a briquetting machine of the roll-press type and then re-briquetting the thus formed briquettes. The green strength of the briquettes of the various examples was found to be satisfactory in each case.

The green briquettes were charged to a horizontal coker in which coking was accomplished principally by radiant heat. A bed of briquettes from 3–5 inches in depth was maintained in the coker grate during the coking. The briquettes were coked at temperatures in the range of about 1050–1450° F., the green briquettes being subjected initially to temperatures in the range of about 1050–1150° F. The amount of material formed during the coking which passed through a standard one-inch Tyler screen was determined and calculated as a percentage of the total coked material. This percentage is tabulated in Table II for each of the examples and is indicative of the comparative coked strength of the briquettes for the various examples.

The coked briquettes were smelted in a small gas-fired, horizontal silicon-carbide retort mounted in a brick furnace. The smelting was conducted at temperatures in the range of about 1850–2350° F. and was continued until zinc evolution had substantially ceased. The dezinced briquettes were removed from the retort, cooled and tested for strength.

The residual strength of the smelted briquettes was determined by rolling individual samples in a 12-inch by 12-inch drum for one minute; the rate of revolution of the drum being 80 revolutions per minute. After thus rolling the samples, the amount of material which was retained on a 1½-inch and on a 1-inch standard Tyler screen, and the amount of material which passed through the 1-inch screen, were determined and calculated as a percentage by weight of the original sample before rolling. These percentages are tabulated in Table III for each example and are indicative of the comparative residual strength of the smelted briquettes.

Table I

| Example No. | Percent Sinter | Percent Coal | Percent Coke | Percent Fire Clay | Percent Bentonite | Percent H <sub>2</sub> O | Percent Oil   |
|-------------|----------------|--------------|--------------|-------------------|-------------------|--------------------------|---------------|
| 1           | 55.3           | 18.4         | 15.7         | 2.8               | 0                 | 3.2                      | 4.6 crude.    |
| 2           | 55.3           | 18.4         | 15.7         | 2.8               | 0                 | 3.2                      | 4.6 residual. |
| 3           | 61.8           | 18.4         | 12.0         | 0                 | 0                 | 3.2                      | 4.6 crude.    |
| 4           | 61.8           | 18.4         | 12.0         | 0                 | 0                 | 3.2                      | 4.6 residual. |
| 5           | 61.8           | 17.4         | 10.2         | 0                 | 2.8               | 3.2                      | 4.6 residual. |

Table II

| Example No. | Percent by Weight of Coked Briquettes Passing through 1-inch Screen |
|-------------|---------------------------------------------------------------------|
| 1           | 6.2                                                                 |
| 2           | 13.2                                                                |
| 3           | 23.7                                                                |
| 4           | 31.2                                                                |
| 5           | 4.8                                                                 |

Table III

| Example No. | Percent Retained on 1½-inch Screen | Percent Retained on 1-inch Screen | Percent Passing Through 1-inch Screen |
|-------------|------------------------------------|-----------------------------------|---------------------------------------|
| 1.....      | 66.7                               | 4.2                               | 29.1                                  |
| 2.....      | 58.0                               | 7.1                               | 34.9                                  |
| 3.....      | 40.5                               | 3.0                               | 56.5                                  |
| 4.....      | 16.0                               | 0.0                               | 84.0                                  |
| 5.....      | 30.2                               | 7.2                               | 62.6                                  |

It will be noted that the coked strength of the briquettes of the present invention, as well as that of those in which oil and a bentonite clay were used as a binder, is superior to that of the briquettes which contained no clay. It will be noted further that the residual strength of the briquettes of the invention is vastly superior to that of briquettes in which no clay or oil and bentonite clay are used as a binder.

Comparable results are obtained with so-called high grade bituminous coking coal, such as Connellsville coal, as well as with lower grade bituminous coking coal known as "lean" coking coal; the Rosita coal of the examples being in this latter category. Thus, for example, comparable results are obtained with lean bituminous coking coal of the type found in the Rocky Mountain area of the United States, and Australia. These bituminous coking coals vary in their degrees of leanness; the Rocky Mountain coal being generally considered in the art to be most lean.

What is claimed is:

1. In a zinc smelting process involving the steps of forming green metallurgical briquettes comprised of an intimate mixture of a sub-divided oxidic zinciferous material, a ground bituminous coking coal and a binder material, coking the green briquettes, passing a vertical col-

umn of the coked briquettes downwardly through a smelting zone in a vertical retort and smelting the coked briquettes in said smelting zone to remove zinc values from the coked briquettes as metallic zinc vapor, the improvement comprising the step of forming said green briquettes with a binder material comprising a plastic kaolinitic-base clay having a softening point in excess of 2000° F. and a mineral oil having a viscosity of about 200 to 1000 seconds, Saybold-Fural, at 122° F., whereby coked briquettes of enhanced strength are obtained in said coking step and a reduced amount of fines are formed during said smelting step.

2. A process according to claim 1 in which a lean bituminous coking coal of a type equivalent at least to a Rocky Mountain bituminous coking coal is used in forming said green metallurgical briquettes and said clay is a fire clay.

3. A process according to claim 2 in which said green metallurgical briquettes contain 15 to 40% of said bituminous coking coal, 0 to 25% of a solid diluent material, 2 to 7% water, 1 to 6% of said clay, 2 to 7% of said mineral oil, and the remainder an oxidic zinciferous material.

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