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PREPARATION OF COKED AGGLOMERATES

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This invention relates to the reduction of zinciferous material and is more especially concerned with that method of reduction in which the charge consists of coked agglomerates of mixed zinciferous material and carbonaceous material. The invention aims to provide certain improvements in the preparation of such coked agglomerates.

It has heretofore been found that coked agglomerates of mixed zinciferous and carbonaceous materials constitute a peculiarly advantageous charge for vertical zinc distillation retorts. Such agglomerates must not split up during coking and must possess satisfactory residue strength, i. e., sufficient strength to pass progressively through the vertical retort without breaking down or sanding, thereby preserving throughout the entire reducing operation that desirable uniform porosity of the charge which enables economic and efficient transfer of heat by hot gases from the hot wall of the retort to the center or core of the charge.

These agglomerates are prepared by first crushing the ore and coal separately, then kneading them together, in a Chilean mill or edge-runner to form a mixture that is suitable for agglomerating. The Chilean mill or edge-runner is frequently referred to as a "chaser", its operation as "chasing", and the treated material as having been "chased". A binder, if necessary, such as sulfite liquor, may be added during the treatment in the edge-runner. The mixture thus prepared in the edge-runner is then agglomerated and coked, at temperatures insufficient to cause any substantial loss of zinc.

The appropriate control of the preparation of the charge for agglomeration involves a proper adjustment of at least the following three factors: (1) nature of the coal with particular reference to its coking characteristics; (2) particle size of (*a*) the zinc ore and (*b*) the coal, before they are kneaded together in the edge-runner; (3) particle size of the mixture of zinc ore and coal, after treatment in the edge-runner, in the final stage of its preparation for agglomeration. These three factors may be appropriately controlled in combination, to secure a firm agglomerate consisting of a coke structure intimately bonded with and enveloping the particles of zinc ore, so as to prevent both splitting up of the agglomerates during coking and disintegration during the subsequent distillation or reduction step.

The carbonaceous material used to prepare the agglomerates should be composed in part of a so-called "free-flowing" coal, i. e., a coal that during coking softens to a great extent, wetting the individual particles of ore, so that when the coke hardens substantially each ore particle is enveloped in and in intimate contact with coke; and, when the ore particles are later disintegrated by the expulsion of their zinc content during the distillation the gaps left in the structure are as small as possible, so that the strength of the residue is preserved. However, such free-flowing coals as a rule swell or puff up when heated to coking temperatures, and are then known as swelling coals. This property of swelling is undesirable in the preparation of coked agglomerates of zinc ore and coal, since the swelling tends to split up the agglomerates during the coking operation. This tendency of the swelling free-flowing coal to split up the briquettes may be overcome by appropriate blending with a coal that does not swell during coking. This non-swelling coal need not necessarily be free-flowing; indeed, even non-coking carbonaceous material, such as anthracite coal dust and coke breeze or the like may advantageously form part of the blend.

The inclusion of anthracite dust coal in the agglomerate mixture serves to maintain the coke structure and give residue strength during the zinc distillation operation. Crushed coke, coke breeze, and similar non-coking carbonaceous materials may be substituted for the anthracite dust coal.

The particle size of both the ore and the coal affects the intimacy of contact of the ore and coal brought about by the subsequent treatment in the edge-runner, as well as the capacity of compacting thus brought about. In general, at least 50% of both the zinciferous material and the carbonaceous material

should be of a graded particle size between 14 and 100 mesh.

Optimum results appear to be secured when the bituminous coking coal is of a graded size with not more than about 16% on a 14 mesh screen and not more than about 17% through a 200 mesh screen, the coal remaining on intermediate screens displaying a substantially uniform gradation of size. The following data may be considered for illustrative purposes.

Bituminous coal hammer mill crushed

	Per cent on	Per cent through
8 mesh screen	4.3	95.7
14 mesh screen	11.8	83.9
20 mesh screen	10.6	73.3
28 mesh screen	9.6	63.7
35 mesh screen	11.8	51.9
48 mesh screen	8.9	43.0
65 mesh screen	7.5	35.5
80 mesh screen	3.6	31.9
100 mesh screen	4.6	27.3
150 mesh screen	5.8	21.5
200 mesh screen	5.0	16.5

It is desirable, but not necessary, that the non-coking carbonaceous material of the agglomerate mixture be of the aforementioned graded particle size, and the closer this is approximated the more closely will the coked agglomerates approximate the optimum desired properties. Coke crushed to pass through 8 mesh has, however, been successfully used for the non-coking carbonaceous material.

The present invention is primarily concerned with the production of coked agglomerates from such finely divided zinciferous material as roasted flotation concentrates and the like, which have, prior to flotation and roasting, been crushed to a size that is too fine for securing the appropriate treatment in the edge-runner. If such extremely fine material, e. g., a roasted concentrate with 30 to 40% through a 200 mesh screen, be subjected to the edge-runner treatment together with the requisite coal, the resulting briquettes will be too dense and will tend to split up during the subsequent coking (by the method heretofore indicated) unless the coking is carried out at an uneconomically slow rate.

I have found that coked agglomerates of improved physical properties can be secured by sintering the roasted zinciferous flotation concentrates. Accordingly, my present invention involves sintering the very finely divided zinciferous material as a preparatory step to the production of coked agglomerates therefrom. Where the finely divided zinciferous material is a zinc flotation concentrate, it is first roasted. The roasting operation may be conducted in any appropriate manner as, for example, in a furnace of the multiple hearth type, in a Hegeler furnace, or the like. Preferably, the roasting is carried on until the sulfur content of the concentrate is around 2–3%, or less. If desired, however, higher percentages of sulfur may be left in the roasted concentrate, say up to 6 to 8%.

The roasted concentrate is mixed with an appropriate amount of fuel for the sintering operation. For this purpose, about 6 to 12% by weight of an appropriate combustible agent, such as carbonaceous material or sulfur, or a combination of both, should be associated or admixed with the roasted concentrate. Where the sulfur content of the roasted concentrate is around 2–3%, I preferably mix therewith from 4 to 12% of anthracite coal dust, coke breeze, or the like, to supply the necessary fuel for the sintering operation.

The roasted concentrate and associated combustible agent is then subjected to a sintering operation preferably by blast roasting. This operation I prefer to conduct on a Dwight-Lloyd sintering machine of the down-draft type. The sintering temperature is sufficiently high to break down the metal sulfates present in the concentrate, such, for example, as magnesium sulfate, calcium sulfate, zinc sulfate, etc. These sulfates are reactive towards the carbonaceous material of the agglomerate mixture during coking and therefore deleteriously affect the coking operation. Accordingly, their elimination in the course of the sintering operation is one of the advantages of the invention.

If the roasted zinc flotation concentrate has been sintered only once, the sinter cake may be fed directly to the edge-runner without preliminary crushing. In case the material has been given a double sintering treatment, that is sintered twice, it is advantageous, before feeding it to the edge-runner, to crush it to approximately the following screen analysis:

Screen analysis of twice sintered roasted concentrate after once through a set of rolls

	Per cent on	Per cent through
8 mesh screen	1.2	98.8
14 mesh screen	8.3	90.5
20 mesh screen	8.2	82.3
28 mesh screen	8.5	73.8
35 mesh screen	11.9	61.9
48 mesh screen	10.3	51.6
65 mesh screen	13.3	38.3
80 mesh screen	5.0	33.3
100 mesh screen	7.1	26.2
150 mesh screen	8.3	17.9
200 mesh screen	5.7	12.2

The porous ore particles produced by sintering are blended by the edge-runner with the coal in such a manner that briquettes formed from the mixture are not so dense as to split up during the subsequent coking operation, and yet the contact between the ore and coal is sufficiently intimate to prevent disintegration of the briquettes during the subsequent distillation or reduction step.

The particle size of the mixture of ore

and coal after treatment in the edge-runner is also of importance. The chased material should have a particle size that is consistent with the formation of an agglomerate of optimum or at least adequate coking and residue strengths. Thus, if the particle size of the chased material is too fine, the agglomerates will be relatively dense and compact. During the subsequent coking, the volatile constituents will tend to split up the agglomerates when they are volatilized. In order to drive the volatile hydrocarbons from the agglomerate, considerable pressure will be set up within the agglomerate. Stresses and strains take place within and the agglomerate will usually rupture and disintegrate. Such a result works away from porosity of the charge, is therefore harmful, and should be avoided.

On the other hand, if the particle size of the chased material is too coarse, the agglomerates will not be as dense and compact as they should be to insure adequate, let alone optimum, coking and residue strengths. In other words, there appears to be a happy mean of particle size for the chased material which is compatible with the formation of an agglomerate that will have adequate or optimum coking and residue strengths.

The following table gives data illustrating the proper size of a chased mix of 60% sintered roasted zinc flotation concentrate, 20% free-flowing coal of bituminous rank mined from the Pittsburg seam of the Monongahela series in the Preston-Taylor Mining District, Taylor County, West Virginia, and 20% anthracite dust coal:

Screen analysis of chased mix

	Per cent on	Per cent through
8 mesh screen	0.7	99.3
14 mesh screen	2.8	96.5
20 mesh screen	4.1	92.4
28 mesh screen	4.1	88.3
35 mesh screen	5.9	82.4
48 mesh screen	4.7	77.7
65 mesh screen	5.3	72.4
80 mesh screen	3.3	69.1
100 mesh screen	4.6	64.5
150 mesh screen	8.3	56.2
200 mesh screen	6.4	49.8

Very satisfactory agglomerates have also been obtained with the following mixtures:

I. 50% sintered roasted zinc flotation concentrate
33% Preston-Taylor coal
17% anthracite dust coal

II. 54% sintered roasted zinc flotation concentrate
28% Preston-Taylor coal
18% anthracite dust coal

In general, the mixture may vary within the following limits:

Sintered roasted zinc flotation concentrate
50–60%
Free-flowing coal, such as Preston-Taylor
35–20%
Anthracite dust coal 15–20%

The graded particle size of the ingredients of the agglomerate mixture insures such density of the mixture as will give adequate if not maximum strength of the coked agglomerate. This graded particle size furthermore promotes the desired intimate mixture of the zinciferous and carbonaceous materials and insures better compacting of these materials by briquetting, extrusion and like operations. Where the agglomerate mixture is too dense, cracking or rupturing of the agglomerates is liable to take place during the coking operation, and if the mixture is not dense enough the coked agglomerates are deficient in strength, particularly in residue strength during the subsequent reduction operation. The graded particle sizes herein contemplated produce a mixture of adequate or optimum density with respect to the desired ultimate properties of the coked agglomerates.

The chased material is suitably agglomerated by briquetting, extrusion, or the like. In this connection, it may be advisable to use a binder in appropriate amounts. The agglomerates may be formed in various sizes and shapes and with varying degrees of density and compactness. Such factors as size, shape and density of the agglomerates will be largely governed by the particular coking and reduction operations to be employed. Other conditions being equal, the longer the column of agglomerates placed in a coking and in a reduction retort, the stronger should be the agglomerates near the bottom of the column to avoid breaking down by compressive forces. Any suitable apparatus may be employed for both the coking and reduction operations. In the present preferred practice of the invention, the agglomerates are coked by direct heating and the coked agglomerates are then smelted for the recovery of their zinc content in an externally heated vertical retort.

I claim:—

1. The method of preparing coke agglomerates of finely divided zinciferous material and carbonaceous material which comprises subjecting the zinciferous material to a sintering operation, intimately mixing the sintered zinciferous material with the carbonaceous material, forming the resulting mixture into agglomerates, and subjecting the agglomerates to a coking operation.

2. The method of preparing coked agglomerates of roasted zinc flotation concentrates and carbonaceous material which comprises subjecting the concentrate to a sintering operation, intimately mixing the sintered concentrate with the carbonaceous material, forming the resulting mixture by pressure into

agglomerates, and subjecting the agglomerates to a coking operation.

3. The method of preparing coked agglomerates of finely divided zinciferous material and carbonaceous material which comprises subjecting the zinciferous material to a sintering operation, intimately mixing the sintered zinciferous material with the carbonaceous material, the carbonaceous material being made up of about equal parts by weight of a free-flowing coal of good coking quality and a non-coking carbonaceous material, forming the resulting mixture by pressure into agglomerates, and subjecting the agglomerates to a coking operation.

4. The method of preparing coked agglomerates of finely divided zinciferous material and carbonaceous material which comprises subjecting the zinciferous material to a sintering operation, intimately mixing the sintered zinciferous material with the carbonaceous material, the carbonaceous material being made up of a substantial proportion of a free-flowing coal of good coking quality, forming the resulting mixture by pressure into agglomerates, and subjecting the agglomerates to a coking operation.

5. The method of preparing coked agglomerates of finely divided zinciferous material and carbonaceous material which comprises subjecting the zinciferous material to a sintering operation, intimately mixing the sintered zinciferous material with the carbonaceous material, the carbonaceous material being made up of a substantial proportion of a free-flowing coal of good coking quality and at least 50% of both the sintered zinciferous material and the carbonaceous material being of a graded particle size between 14 and 100 mesh, forming the resulting mixture by pressure into agglomerates, and subjecting the agglomerates to a coking operation.

6. The method of preparing coked agglomerates of roasted zinc flotation concentrates and carbonaceous material which comprises subjecting the concentrate to a sintering operation, intimately mixing the sintered concentrate with the carbonaceous material, the carbonaceous material being made up of about equal parts by weight of a free-flowing coal of good coking quality and an non-coking carbonaceous material and at least 50% of both the sintered concentrate and the carbonaceous material being of a graded particle size between 14 and 100 mesh, forming the resulting mixture by pressure into agglomerates, and subjecting the agglomerates to a coking operation.

7. The method of preparing coked agglomerates of finely divided zinciferous material and carbonaceous material which comprises agglomerating an intimate admixture of sintered zinciferous material and coal, said coal consisting of a blende of free-flowing coking coal and non-coking coal in conjunction with the sintered zinciferous material adapted to provide agglomerates that will not swell and disintegrate when heated, and subjecting the agglomerates to a coking operation.

In testimony whereof I affix my signature.

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