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SMELTING ORES OR THE LIKE.

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To all whom it may concern:

Be it known that I, LUDWIG HEINRICH DIEHL, a subject of Germany, residing in Darmstadt, Germany, have invented certain new and useful Improvements in Smelting Ores or the like (for which I have filed applications in Germany March 12, 1919, Serial No. D. 35,543 VI/40a, September 15, 1919, Serial No. D. 36,404 VI/40a, and Great Britain March 12, 1920, Serial No. 6,446, and July 12, 1920, Serial No. 208,885), of which the following is a specification.

The present invention relates to improvements in the preparation and smelting of ores, roaster-residues, slags and the like containing iron and zinc, for the separation and recovery of these metals in commercially useful forms.

It is well known that when zinc-bearing iron ores, residues and the like are smelted in blast-furnaces such as are used in making pig-iron, the metallic zinc volatilized from the charge gives rise to deposits and incrustations in the throat and gas pipes of the furnace, forming obstructions which at times cause great trouble. Sometimes the zinc penetrates into the joints of the brick-work where, becoming gradually oxidized, it increases in volume and tends to displace the brick-work. Large quantities of zinc-bearing iron ores, residues and the like are available which, on account of their containing appreciable quantities of zinc or both zinc and sulphur, have hitherto been regarded as unsuitable or even worthless for smelting in blast-furnaces.

The chief objects of the present invention are to prepare such zinc-bearing materials in a form chemically and physically suitable for treatment in the blast-furnace and then by smelting them with suitable additions to separate and recover the iron and zinc without the drawbacks referred to, substantially the whole of the zinc in the charge being volatilized and carried out of the furnace by the current of gas as an unobjectionable compound which is recovered as a useful product while the iron is tapped off as molten metal to yield pig-iron or other ferrous product of good quality.

According to the invention the raw material employed (viz, the ore, roaster-residue, slag or the like, or mixture of such materials, containing iron and zinc, and hereinafter termed "ore"), if it contains sulphur, is first desulphurized, and, if it be too fine for blast-furnace work, is brought into suitable physical form by sintering, briquetting, or otherwise. Since it must, when charged into the furnace, contain enough iron to yield molten metal in quantity sufficient to enable the latter to be tapped in the usual way, any deficiency in iron is rectified by the addition of suitable materials, such as iron ore or scrap iron. It is then smelted in the usual manner in a blast-furnace along with the usual reducing and fluxing agents (coal or coke, limestone and the like) and other materials if desired, and in presence of a chloride. The presence of a chloride is most easily procured by mixing with the charge a chloride in suitable proportions, in which case an alkali chloride, an alkaline earth chloride, zinc chloride or a mixture of such chlorides is most suitable, being less easily volatile or decomposable at the temperature of the upper part of the blast furnace than most other chlorides, and being free from metals which might pass into the iron produced and impair its quality. The zinc present in the charge is thus volatilized, probably as chloride or oxychloride, and carried out of the furnace by the gas, while the iron and slag are obtained in a molten condition free or practically free from zinc. The iron is tapped off and may be used directly for steel-making, cast into pig-iron, or otherwise utilized. The zinc compound is collected from the gas in any convenient manner; it may, for example, be recovered partly in the flue dust and partly in the gas-washing plant, this method having the advantage that a clean combustible gas, similar to ordinary blast-furnace gas and suitable for use in gas-engines or for heating purposes, may be obtained. The nature and proportions of the fuel, fluxing materials and other additions (if any) in the charge are chosen with regard to the composition of the ore and kind of iron to be produced, in the manner well understood in ordinary blast-furnace practice; by suitable selection of these a typical blast-furnace slag, containing only about 0.1 per cent of zinc and adapted to be run off in the usual manner, can be obtained.

The quantity of suitable chloride to be added to the charge depends upon the amount of zinc present and may be in the proportion of about 2 atoms of combined

chlorine to 1 atom of zinc present in the ore. I have discovered, however, that zinc oxide can be volatilized somewhat readily along with zinc chloride if it be heated together with the latter compound in a current of blast-furnace gas, and that a smaller proportion of chloride than that just mentioned is therefore sufficient for carrying out the process satisfactorily, especially when the charge is very rich in zinc. The reduction in the proportion of chloride must not be carried too far, since a pronounced shortage of chloride would lead to the volatilization of metallic zinc and the troubles indicated above would tend to arise in greater or less degree. It is best so to regulate the amount that the zinc product carried out of the furnace contains little or no metallic zinc; for example the zinc product deposited in the settling ponds of the gas-washing plant should develop therein only a small amount if any of hydrogen gas.

In smelting the ore with the addition of suitable chloride as described, the formation of incrustations in the furnace and pipes is reduced to a minimum, as the zinc—being in a more volatile form than heretofore—is carried almost entirely into the flue dust or the gas-washers. The volatilized zinc compound while being carried by the gas current is exposed to the action of the lime, alkali and moisture therein; it is also exposed to the action of alkali in the gas-washer—the water in which is normally alkaline and for the purpose of this invention is if necessary kept slightly alkaline by the addition of lime or suitable alkali—and the zinc is thus collected in the wash-water as basic carbonate or the like, the combined chlorine which was present in the volatilized compound passing into solution as alkali chloride or alkaline-earth chloride. The crude precipitate, contaminated with coke dust, flue dust and other impurities, may be allowed to subside in the settling ponds, collected by filtration or otherwise, washed with water to remove soluble substances and then calcined to eliminate combustible and volatile impurities and to render the otherwise comparatively voluminous product denser. It then consists of crude zinc oxide, which may be utilized in any desired manner.

The solutions of chlorides of the alkalis or alkaline-earths obtained in the gas-washing plant can be evaporated and the concentrated product used as suitable chloride for fresh operations in the furnace.

The invention is particularly applicable to the treatment of the roaster-residues produced from zinciferous pyrites. As is known, the residue obtained on burning such pyrites in roaster furnaces for the manufacture of sulphuric acid retain a fairly large proportion of sulphur, which may be as much as 5 to 8 per cent. I prefer to desulphurize, sinter and smelt such residues in the following manner. The residue is crushed to about one-quarter inch size and roasted (preferably in rotary kilns about 60 metres in length by about 2½ to 3 metres in diameter or in other mechanically-operated furnaces) with fuel and a limited supply of air so that a portion—say one fourth part—of the ferric oxide present is reduced to ferrous oxide. The enhanced fusibility of the product allows it to become sintered while desulphurization is taking place. The quantities of fuel (coal, coal-dust, coke, oil or gas) and of air used are so regulated that the exit gas contains about 3.5 to 5.5 per cent by volume of SO_2, 6 to 9 per cent of CO_2, and 8 to 11 per cent of O, and the sulphur in the residue is reduced to 0.5 per cent or less. In order to obtain with a rotary kiln the best results as regards strength of gas, reduction of sulphur contents of the ore and sintering of the latter into a porous material free from dust, the charge should be heated with a long flame to a final temperature at which the material will just begin to fuse and the quantities of fuel and air should be such that about one fourth part of the ferric oxide is reduced to ferrous oxide. The desulphurization will then be satisfactory and the sintering will take place more easily than on roasting with a large excess of air. The exit gas can be utilized for the manufacture of sulphuric acid or otherwise; if desired it can be rendered richer in SO_2 by adding a proportion of crushed fresh pyrites to the charge before the roasting and sintering operation. The desulphurized and sintered product is then smelted with the addition of suitable chloride as already described, the usual reducing, fluxing and other additions being made according to the composition of the ore and the kind of iron required.

Example.

The following example illustrates the manner in which the invention may be put into practice. The ore used consisted of zinciferous roaster-residue containing 5.02 per cent of sulphur and 41.42 per cent of iron. The desulphurization was carried out in a rotary kiln 60 metres in length and 2½ metres in diameter having a through-put of about 150 tons of residue per 24 hours. For each metric ton (1000 kilos) of residue there were used 65 kilos of coal (containing 66.7 per cent of carbon and 1.5 per cent of sulphur) and 885 cubic metres of air, yielding 910 cubic metres of exit gas containing 3.75 per cent by volume of SO_2, 8.82 per cent of CO_2 and 8.06 per cent of O. The sintered, desulphurized material contained 8.32 per cent of zinc, 0.06 per cent of sulphur and 44.21 per cent of iron (31.85 per cent as

Fe_2O_3 and 12.35 per cent as FeO). The gas leaving the kiln had a temperature in the dust-chamber of 450°–500° C. and was suitable for the manufacture of sulphuric acid. The sintered, desulphurized material was then smelted with the addition of a suitable chloride and reducing, fluxing and other materials appropriate for the production of pig-iron of the quality (in this case, high-manganese iron) desired. Here were used 1308 tons of sintered material, 146 tons of rock salt (sodium chloride), 2295 tons of coke, 897 tons of limestone, 278 tons of scrap iron and 278 tons of iron in the form of manganiferous iron ore containing 75 tons of Mn. There were produced 1046 tons of pig-iron (containing no zinc, 3.25 per cent Mn, 1.67 per cent Si, 3.68 per cent C, 0.038 per cent S, and 0.170 per cent P), 1125 tons of slag containing 0.10 per cent of zinc, and 158 tons of flue dust containing 21 tons of zinc (existing mainly as oxide, oxychloride or the like). The zinc compound carried in the gas was washed out in the gas-washing plant of the furnace; the product was collected from the settling ponds by filtration, washed, and calcined at a low red heat to drive out combined water, carbon dioxide and a small quantity of combined chlorine. It then weighed 125 tons and contained 66.3 per cent of Zn=82.5 per cent of ZnO. The flue dust was briquetted and returned to the furnace. The gas from the washing plant consisted of good, clean, blast-furnace gas suitable for use in the ordinary manner.

From the foregoing example it will be seen that the invention affords a practical method of treating roaster-residues so as to effect a clean separation of the valuable constituents thereof, with recovery of the iron, zinc, and (if desired) the sulphur and combustible gas, all in a commercially useful form, and with simultaneous elimination of blast-furnace slag of the usual type substantially free from zinc.

The invention is also applicable to zinc and iron bearing ores and the like which are either naturally free from sulphur or are procurable in a desulphurized condition. In such cases if the ore is too fine to be charged directly into the blast-furnace it is first agglomerated or briquetted in any suitable manner and if necessary any deficiency in iron is made good as already indicated. It is then smelted with the aid of suitable chloride and other additions as hereinbefore described.

Having thus fully described the nature of the said invention and the best means I know of carrying the same into practical effect, I claim:—

1. The treatment of zinciferous iron ores or the like adapted to be smelted in a blast furnace to obtain pig-iron, which treatment consists in smelting the ore in a blast furnace in presence of a chloride along with the appropriate fluxing and other ingredients of a blast-furnace charge, tapping off the molten iron produced and collecting the volatilized zinciferous material carried out of the furnace by the gases.

2. The treatment of zinciferous iron ores or the like adapted to be smelted in a blast furnace to obtain pig-iron, which treatment consists in smelting the ore in a blast-furnace in presence of a chloride along with the appropriate fluxing and other ingredients of a blast-furnace charge, tapping off the molten iron produced, collecting by means of alkaline wash-water the volatilized zinciferous material carried out of the furnace by the gases, and washing and calcining the zinciferous product.

3. The treatment of zinciferous iron ores or the like adapted to be smelted in a blast furnace to obtain pig-iron, which treatment consists in agglomerating them into a form suitable for blast-furnace practice, smelting them in a blast-furnace in presence of a chloride along with the appropriate fluxing and other ingredients of a blast-furnace charge, tapping off the molten iron produced and collecting the volatilized zinciferous material carried out of the furnace by the gases.

4. The treatment of zinciferous iron ores or the like adapted to be smelted in a blast furnace to obtain pig-iron, which treatment consists in agglomerating them into a form suitable for blast-furnace practice, smelting them in a blast-furnace in presence of a chloride along with the appropriate fluxing and other ingredients of a blast-furnace charge, tapping off the molten iron produced, collecting by means of alkaline wash-water the volatilized zinciferous material carried out of the furnace by the gases, and washing and calcining the zinciferous product.

5. A process of winning zinc compounds from sulphur-free zinciferous and ferruginous ores or the like, which consists in volatilizing the zinc as a compound by smelting the ore in a blast furnace in presence of a chloride and collecting the zinciferous material carried out of the furnace by the gases.

In testimony whereof I have signed my name to this specification.

LUDWIG HEINRICH DIEHL.