Patented Sept. 2, 1941 2,254,660

UNITED STATES PATENT OFFICE

2,254,660

TREATMENT OF FERRIFEROUS ORES

Karl Koller and Zsigmond Gálocsy, Budapest, Hungary

No Drawing. Application August 13, 1940, Serial No. 352,405. In Germany November 7, 1938

1 Claim. (Cl. 75—41)

This invention relates to the blast furnace process and more particularly to a process for the reduction of the amount of sulphur contained in blast furnace charges.

It is known that in the blast furnace process the ores and fuels charged to the furnace almost always contain a certain proportion of sulphur, by which the metal produced is contaminated unless special steps are taken to withdraw this sulphur from the metal. This can be accomplished in the blast furnace itself by means of a basic slag or, if an acid slag is employed, in an apparatus beyond the blast furnace with the aid of alkalis, such as soda, for example by the process of Prof. Paschke-Peetz. The operation of the blast furnace, however, is rendered substantially more expensive by these additional steps.

The present invention aims at effecting desulphurization in the blast furnace process while completely or partially eliminating these additional steps, and thereby reducing the cost of the blast furnace process and simplifying the same.

The invention is based on the discovery that the amount of sulphur introduced into the blast furnace by the charge consisting of a mixture of ferriferous ores, coke and fluxes need not be removed only after the mass has already been melted, but can be removed, at least in part, from the charge itself before melting.

To this end, the present invention contemplates the per se known introduction of steam into the blast furnace. However, in contradistinction to known proposals, according to which the steam is supplied to the lower portion of the blast furnace, where it enters into an endothermic reaction (water gas reaction) with the incandescent solid fuel, the present invention contemplates superheating the stea to be introduced to about 400 to 800° C. an supplying said steam to a zone of the furnace situated above the highest temperature smelting zone, the temperature of which corresponds with that of the superheated steam, so that, while the water gas reaction is substantially avoided, reactions in the gaseous phase are predominantly initiated thereby in the furnace, the steam being partly reduced to hydrogen during the exothermic reaction with the upwardly flowing carbon monoxide of the blast furnace gases, particularly owing to the catalytic action of the iron oxide, while the resulting nascent hydrogen and also the undecomposed steam convert a large portion of the sulphur present in the charge into gaseous sulphur compounds, such as hydrogen sulphide, which pass out with the blast furnace gases.

Since a substantial portion of the sulphur present in the blast furnace charge is combined and removed by the process of the present invention before reaching the lower zones of the furnace, further desulphurization steps can be dispensed with in the case of fuels and ores low in sulphur. Given a charge of normal sulphur content, the slag can have a substantially lower basicity than customarily, and even when working with an acid blast furnace slag, after-desulphurization of the iron can be entirely or largely dispensed with, despite the acidity of the slag. The process of the present invention also enables the use in the blast furnace process of types of coke or ores relatively high in sulphur (containing up to about 2 to 3% of sulphur) which hitherto were practically unusable in the blast furnace process precisely because of their high sulphur content.

By introducing steam superheated up to about 400 to 800° C. into the upper zones of the blast furnace, the advantage is also obtained that in addition to the partial desulphurization of the charge, a portion of the heat required for preheating the charge is covered by the sensible heat of the steam, as well as by the exothermic reaction:

$$H_2O+CO=CO_2+H_2$$

which takes place. In consequence, the requirement of coke becomes smaller, thus affording the additional advantage that less lime has to be consumed for slagging of the ash constituents of the coke. When the amount of slag to be melted is smaller, moreover, the requirement of coke is once again reduced by a further small amount.

If, however, the addition of coke is not reduced, despite the smaller requirement, a higher temperature will result in the hearth of the blast furnace, whereby the pig iron produced will be higher in manganese and silicon for a given mixture of ore plus flux. If the acid smelting process, in which precisely because of the acid slag a very high loss of manganese must be expected, is employed for types of iron rich in manganese, the process of the present invention has a favourable effect in that the higher temperature thereby attained counteracts loss of manganese in the slag.

The superheating of the steam to be introduced into the blast furnace can in principle be carried out in any desired manner, for instance in heat exchangers.

It is advantageous, however, to effect the superheating in the manner described in our prior U. S. patent specification No. 1,964,207 and in our U. S. patent application Ser. No. 202,926 which has matured into Patent No. 2,219,046, Oct. 22, 1940, in a combustion chamber connected ahead of the blast furnace.

The advantages of the process according to the invention are explained in greater detail with reference to the following specific example.

Suppose that the output of a certain blast furnace amounts to 240 metric tons of pig iron per day. The following quantities of materials are being fed into the blast furnace per metric ton of pig iron:

1950 kg. of ore having a content of Fe of 46.6%
925 kg. of coke having a content of C of 85%, and a content of ash of 10%, and
425 kg. of limestone.

This charge introduces a quantity of 23.6 kg. of sulphur per metric ton of pig iron into the blast furnace.

The quantity of slag amounts to 726 kg. per metric ton of pig iron, and the basicity of the slag is 1.23.

Suppose that the process according to the invention causes 40% of the quantity of sulphur contained in the charge to be converted into gaseous compounds and removed. In this case it will be possible to reduce the quantity of limestone introduced by roughly one-half, so that it will now amount to 210 kg. per metric ton of pig iron. In accordance therewith the quantity of slag will be reduced by about 120 kg., and will amount to only 606 kg. per metric ton of pig iron. In order to enable the above results to be obtained it is necessary to introduce into the blast furnace a quantity, per metric ton of pig iron, of 200 cubic metres of superheated steam having a temperature of about 750° C., one half of which quantity, i. e. roughly 100 cubic metres will enter into reaction with the upwardly flowing carbon monoxide, whereby a quantity of about 100 cubic metres of nascent hydrogen will be produced. In this case the saving in heat, due to introduced and saved quantities of heat, expressed in kilogram-calories (Symbol Cal., 1 Cal. being equal to 3,968 B. t. u.) per metric ton of pig iron will result as follows:

	Calories
1. The quantity of heat introduced into the shaft of the blast furnace by 200 cubic metres of steam amounts to	56,000
2. The quantity of heat generated in the furnace shaft by the conversion of 100 cubic metres of steam (430 Cal. per cubic metre of steam amounts to	43,000
3. A saving in heat results from the reduction of the quantity of limestone charged into the furnace by 210 kg., in consequence whereof the expulsion of the 90 kg. of carbon dioxide contained in 210 kg. of limestone becomes unnecessary, and the quantity of heat that would be required for this purpose (960 Cal. per kg. of CO_2) is saved; this saving amounts to	86,000
4. A saving in heat results therefrom that the quantity of heat required for the melting of 120 kg. of slag (500 Cal. per kg. of slag) becomes unnecessary; this saving amounts to	60,000
5. Owing to the reduction of the quantity of limestone and (in consequence of the saving in heat) of that of coke, which have to be introduced into the blast furnace per metric ton of pig iron, the throughput of the furnace is accelerated and in consequence thereof wall losses are diminished; this diminution may be estimated at the figure of	10,000
Total	255,000

In view of the fact that each kilogram of C, during its combustion to CO, generates 2440 Cal., the process according to the invention will, in the case of the above example, enable a quantity of

$$\frac{255,000}{2,440} = 104 \text{ kg. of C}$$

per metric ton of pig iron to be saved, which quantity of C corresponds to a quantity of coke of 122 kg. Accordingly, the saving in coke amounts to

$$\frac{122 \times 100}{925} = \text{roughly } 13\%$$

As, moreover, the length of time required for the charge to pass through the furnace will be shortened by about 10%, the daily throughput will, in case of employing the process according to the invention, amount to 260 metric tons of pig iron as compared to the 240 metric tons indicated above.

At the same time the basicity of the slag will become reduced from 1.23 to a figure of roughly 1, so that a fairly acid slag will be obtained.

It follows, accordingly, from the above example that the process according to the invention will, in addition to the partial desulphurisation of the charge, make it possible to reduce the necessary quantities of coke and limestone per metric ton of pig iron, to accelerate the throughput of the furnace and also to reduce the basicity of the slag.

What we claim is:

Process for the manufacture of sulphur poor iron comprising charging a mixture of iron bearing ores, coke and fluxes in an air blast furnace, superheating steam outside the furnace to a temperature of 400 to 800° C. under avoidance of dissociation, introducing the undissociated steam exclusively into a zone of the furnace having approximately the temperature of the introduced steam, reducing a part of the steam after its introduction into the furnace by reaction with the upwardly flowing carbon monoxide to hydrogen and converting the sulphur present in the charge by reaction with said hydrogen and with the undecomposed steam into gaseous sulphur compounds.

KARL KOLLER.
ZSIGMOND GÁLOCSY.