

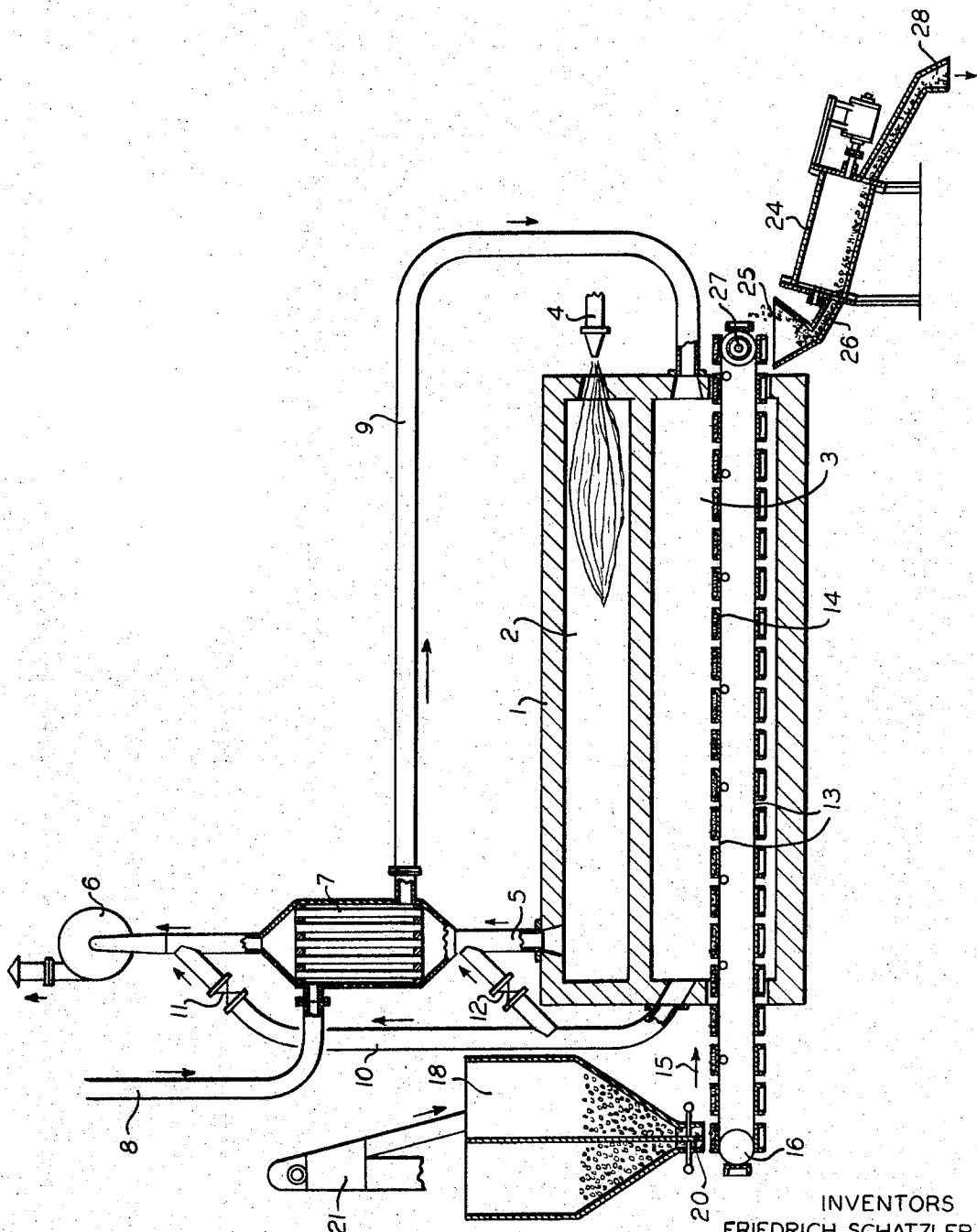
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PROCESS FOR ROASTING MATERIALS CONTAINING CHROMIUM OXIDE

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PROCESS FOR ROASTING MATERIALS CONTAINING CHROMIUM OXIDE**Friedrich Schatzler, Aerzen, and Klaus Falk, Hameln, Germany, assignors to Zahn & Co. G.m.b.H., Hameln (Weser), Germany**

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8 Claims. (Cl. 75—7)

This application relates to a process and apparatus for the alkaline roasting of materials containing chromium oxide.

Two fundamentally different processes are known for the alkaline roasting of chromium ores. In the process hitherto predominantly employed, the ore to be roasted is mixed with an additive, such as alkaline earth metal oxides or carbonates, e.g. lime or dolomite or residues containing iron oxide obtained in the course of further processing of the material to be roasted. The additives impart to the material to be roasted the consistency necessary for roasting in rotary, vertical, circular or overlying-bell kilns. Since the additives figure in the raw material balance, besides unprofitably occupying valuable kiln volume, and must be eliminated in the subsequent processing, attempts have for a long time been made to carry out the roasting process in the absence of additives.

The new process, which operates without additives, cannot be carried out in kilns of the types mentioned above since the material to be roasted becomes viscid at the high roasting temperatures and cannot withstand the mechanical stresses occurring in these kilns. As a result, the material agglomerates or forms deposits upon the kiln walls. This soon interferes with the operation of the kiln and, at the same time, the reactive surface is considerably diminished by the agglomeration, so that reaction may cease rapidly.

The present invention provides a process and an apparatus for the alkaline roasting of chromium ores and of other materials containing chromium oxide which operates without the aforementioned additives and which avoids the disadvantages of the known processes.

This is achieved by a process for the alkaline roasting of materials containing chromium oxide without additives wherein the material to be roasted is pressed into cakes and conveyed, free from mechanical stresses, on a support in counter-current to the flow of the roasting gases, through a long reaction space of small height, in which is maintained a temperature gradient increasing in the direction of advance in said space of the material to be roasted to a maximum temperature less than the melting or sintering temperature of the cakes.

It has been found that the fusible alkali metal oxide or the eutectic mixtures of alkali and pre-formed chromate present in the material to be roasted (mixture of chromium ore and alkali metal carbonate, especially sodium carbonate or caustic alkalis) cannot leave the material to be roasted and thus do not lead to segregation and agglutination when the material to be roasted comprises a non-fusible matrix in which the molten components are immobilized by capillary forces in the void spaces. This matrix is constituted by the gangue of the ores, which varies in composition according to the origin of the ores. It has been found that a matrix of this type is formed only when the material to be roasted is previously compressed mechanically and when the melting point or sintering point of the matrix is not reached in the reaction space. Since the strength of this matrix is naturally low, it must not be subjected to mechanical stresses, such as those produced by agitators or other conveying means, passing through the material to be exploited or strains resulting from gravitational forces in rotary or vertical

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kilns. If the thickness of the layer of the material to be roasted is too great, its own weight suffices sometimes to cause the melt to run out. This determines an optimum roasting temperature for a given ore. Precise control of temperature and of the temperature gradient is important for successful execution of the process.

The material to be roasted, which consists of a mixture of the material containing chromium oxide and alkali metal carbonate or caustic alkali, is compressed, if desired, with addition of small amounts of water, before it is loaded into the roasting furnace. Advantageously, shaped bodies having a material thickness of up to 50 mm., preferably 10 to 50 mm., are formed in a mechanical press. These thickness limits are determined by the diffusion velocity of the oxidizing gas in the material to be roasted, which is, in turn, dependent upon the pore diameter, the partial pressure of oxygen, the optimum temperature and time.

A further characteristic of the process of the invention is the flow of the roasting gas, which must be in counter-current in the advance of the material to be roasted. The CO_2 formed as by-product of the reaction must be removed as soon as possible after its formation, to prevent it from adversely affecting the course of the reaction by equilibrium formation. The flow velocity of the roasting gas is from 1 to 10 m./sec., and thereby a good heat distribution is achieved. This in turn implies a small free cross-section of gas flow and thus a small distance between the material to be roasted and the roof of the reaction space.

These conditions can be successfully met only by a long, indirectly-heated reactor space of small height, in which a temperature gradient is maintained increasing in the direction of advance of the material to be roasted to a maximum below the melting or sintering temperature of the internal matrix of the molded mass. A suitable embodiment is, for example, a tunnel furnace having a reaction and a firing space, which are separated from each other by a wall, having a substantially horizontal support surface for the material to be roasted. The support surface may, if desired, comprise several consecutive segments and must be displaceable through the furnace without any mechanical stress being placed on the material to be roasted. In other words, the material to be roasted is conveyed horizontally through the roasting space on a mobile support surface in such a manner that it is not subjected to mechanical stress.

It is necessary that the distance between the surface of the material to be roasted and the underside of the partition wall be as small as possible. The roasting gas flows through the gap between the partition wall and the material to be roasted and the cross-section of the gap is preferably such that the flow velocity of the gas is from 1 to 10 m./sec., as stated above. The material to be roasted can be accurately observed during the entire roasting process. Because of the length of the reaction space, the optimum conditions for the progress of the reaction can be created at all points. The material rests on the support surface without any mechanical stress and is separated from this surface only after leaving the furnace, by means of a stripper.

In a known method for the alkaline roasting of chromium ore, pressed shapes are prepared from the chromium ore and soda and are subjected, in a row with intervals for admission of air, to the action of heated air in furnaces, preferably in muffle furnaces, avoiding the entry of flames.

This process was not successful, because the shaping and the indirect heating of the material to be roasted are not, in themselves, enough. To this must be added the feature of the present invention, that the material to be roasted is conveyed, free from mechanical stresses, on a

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support surface in a direction opposite to the flow of the roasting gas, preferably air, through a long reaction space of small height, in which a temperature gradient is maintained increasing in the direction of advance of the material to be roasted.

According to a specific embodiment of the invention, the partition wall between the reaction space and the firing space consists of silicon carbide.

It has been found that silicon carbide bricks possess the necessary intensity of radiation and heat output. These bricks are advantageously impregnated with materials having a high melting point, for example kaolin or the like, so as to reduce their porosity. This prevents damage to the silicon carbide bricks through corrosion by the atmosphere of the reaction space.

Example 1

The furnace employed was a small tunnel furnace, with an effective width of 200 mm. and an effective length of 6000 mm. The supports for the material to be roasted were chamotte plates, conveyed through the oven on rail-guided carriages. The roasting space was separated from the firing space by silicon carbide plates. The oxidizing gas was air, blown through the roasting space at the constant rate of 55 m.³/h., in counter-current to the material to be roasted. The free cross-section of the roasting space was 1 dm.², so that the flow velocity of the gases was about 7 m./sec. The furnace was heated by 8 uniformly-distributed burners. The temperature gradient of the reaction space was observed through five stationary and one mobile thermocouples. The residence time of the material in the roasting zone was 60 minutes, the charge density was 3.7 kg. per carriage. Altogether 10 carriages were in the furnace at one time.

The starting material containing chromium oxide was an Albanian chromium ore with a Cr₂O₃ content of 41.6%. The degrees of milling corresponded to 2% residue on a DIN 100 sieve. The ore was mixed with soda in a molar ratio of 1 Cr₂O₃:2.6Na₂O. This mixture was molded, on a ring roller press, into cakes having a maximum thickness of 25 mm. and an individual weight of 38 g. The mean optimum temperature was found to be 1100° C. A temperature gradient of 1060 to 1120° C. was set up in the furnace.

Continuous, single-pass operation yielded a roasted product with a soluble Cr₂O₃ content of 24.04% and 27.01% total Cr₂O₃, corresponding to a chromium yield of 89.00%.

Example 2

The material containing chromium oxide was a Brazilian ore with a Cr₂O₃ content of 49.8%. The ratio ore:soda was 1 Cr₂O₃:2.0Na₂O. The other conditions were those described in Example 1. The mean optimum temperature for this ore was 1050° C.; a temperature gradient of 1030 to 1070° C. was set up in the furnace. Continuous operation yielded a product with a water-soluble Cr₂O₃ content of 28.69% and 30.48% total Cr₂O₃ content. This corresponds to a 94.06% exploitation of the ore. The yield, calculated on the alkali, was likewise 94.06% and the total raw material yield was 88.47%.

The appended drawing diagrammatically illustrates by way of example, but without limitation, a tunnel kiln for carrying out the process of the present invention. The kiln and the parts used with it are shown in sectional view.

In the kiln shown in the drawing, instead of the rail-guided carriages mentioned in Example 1, an endless chain is used for the transport of the material to be treated, through the reaction space.

In the drawing the tunnel kiln 1 has for indirect heating a combustion chamber of firebox 2 and a reaction space 3. The combustion chamber 2 is heated by a burner 4, which is supplied with fuel by a source not shown in the drawing. The hot combustion gases are sucked off by a ventilator 6 through a tube 5. In said

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tube 5 a recuperator 7 is arranged, through which the oxidizing air sucked in through tube 8, is passed. After passing through recuperator 7, the oxidizing oxygen-containing gas, preferably atmospheric air is passed through a tube 9 at the outlet end of the kiln to the reaction space 3. The oxidizing air flows in counter-current to the material to be reacted, through the reaction space 3 and is sucked off through a tube 10 and the ventilator 6. Tube 10 has two outlet pieces and can be connected in front of and/or behind the recuperator 7 to tube 5, by adjustment of the valves 11, 12.

Through the reaction space 3 of kiln 1 an endless chain 13 is guided, on which spaced cast cups 14 are arranged. These cups may consist also of steel. Instead of the cup-like shape, plates, dishes or trays, or the like, of other shape may also be used. The advancing and the return travel end of the chain are guided in the reaction space so that loss of heat caused by removal of the transport device 13 from the kiln, is reduced to the smallest possible minimum. The transport device consisting of chain 13 is driven in the direction of arrow 15 by a motor not shown in the drawing.

At the inlet opening of the kiln, chain 13 is guided over a roller 16 which is arranged at a distance from the kiln. Above the part of the chain which is outside the kiln means for feeding the material to be reacted are arranged. In the embodiment shown, these means consist of a bunker 18 for storing the material to be reacted. The discharge opening 20 of the bunker 18, which may be controlled by a slide, is located directly above the cups 14 arranged on band 13. Said opening 20 is, in the case of a transport device, provided with several spaced receiving elements, so dimensioned that opening 20 extends in the longitudinal direction of the kiln to a maximum which is equal to the longitudinal dimension of an individual cast cup. In the embodiment shown in the drawing the length of the discharge opening 20 is equal to the length of a cast cup. In the case of a continuous feeding of the band 13, the discharge opening 20 could be permanently open in a manner adjusted to the transport velocity of the band, so that a continuous layer of the material to be reacted is formed.

In the embodiment shown, the slide which controls the discharge opening 20, can be controlled during a continuous movement of band 13, for example by means of stop cams provided on the cast cups, in such manner that opening 20 is open during passage of a cup.

In order to charge bunker 18, for example a bucket conveyer diagrammatically indicated at 21 can be used, into which the necessary amount of the material to be reacted is introduced. Reference symbol 24 denotes a preliminary crushing device, into which the material treated in the kiln is introduced over a funnel 25 and a slide 26. After being reacted in the kiln, the treated material is tilted into funnel 25, due to the deflection of band 13 around roller 27, which is driven e.g. by a driving motor. The reacted material is discharged from the preliminary crushing device 24, which may be formed e.g. as a drum, over a chute 28, for being further processed. The transport devices used are driven by conventional driving motors.

The parts and percent stated herein are by weight if not otherwise stated.

We claim:

1. A process for the alkaline roasting of materials containing chromium oxide by means of roasting gases essentially consisting of forming a mixture of said materials with a compound selected from the group consisting of sodium carbonate and caustic alkali, molding the resulting mixture into cakes and conveying the cakes, free from mechanical stresses, on a support, in counter-current to the flow of said roasting gases, through a heated long reaction space of small height, in which is maintained a temperature gradient increasing in the direction of advance of the material to be roasted, up to a maximum tempera-

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ture which is less than the melting and sintering temperature of the cakes.

2. A process as claimed in claim 1, wherein the flow velocity of the roasting gas is from 1 to 10 m./sec.

3. A process as claimed in claim 1, wherein the thickness of the individual cakes is up to 50 mm. 5

4. A process as claimed in claim 3, wherein the thickness of the individual cakes is in the range of 10-50 mm.

5. A process as claimed in claim 1, wherein the roasting process is carried out in a tunnel or canal furnace comprising a reaction space and a firing space, said reaction space and firing space being separated by a wall. 10

6. A process as claimed in claim 5, in which the separating wall consists of silicon carbide.

7. A process as claimed in claim 6, wherein the wall 15

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comprises silicon carbide bricks impregnated with a material having a high melting point.

8. A process as claimed in claim 1, in which the roasting gas is atmospheric air.

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