

[54] **PROCESS AND DEVICE FOR THE
QUANTITATIVE ANALYSIS OF FREE LIME**

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23/253 R, 259[56] **References Cited****UNITED STATES PATENTS**

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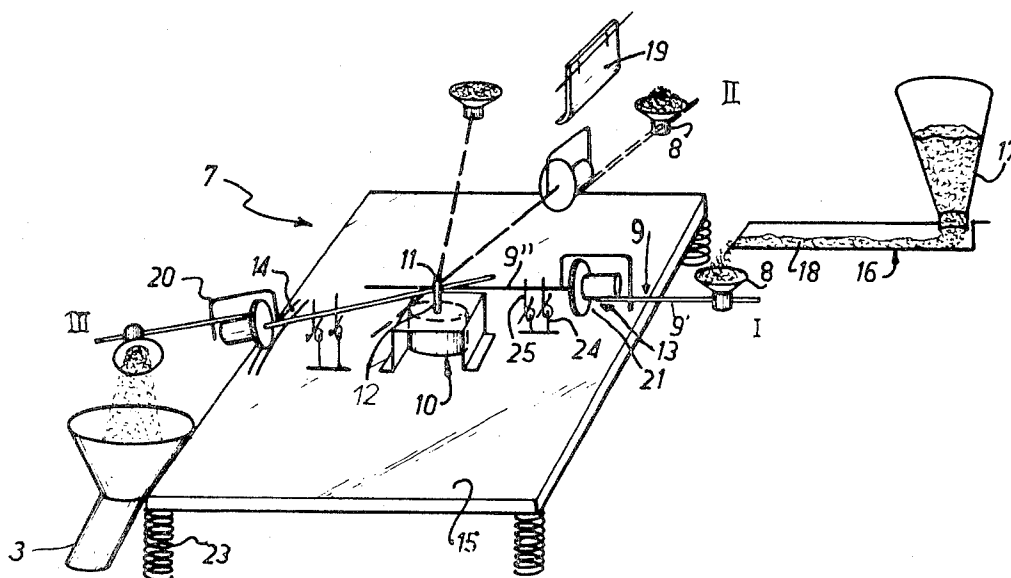
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[57] **ABSTRACT**

A process for the quantitative analysis of the free lime content of a sample of powder, in which a given quantity of the powder is mixed with a given quantity of reagent in a container, characterized by the fact that analysis is done in this container, and consists of conductimetric, potentiometric, pH-metric or similar methods, the said container being heat-regulated if necessary.

12 Claims, 4 Drawing Figures

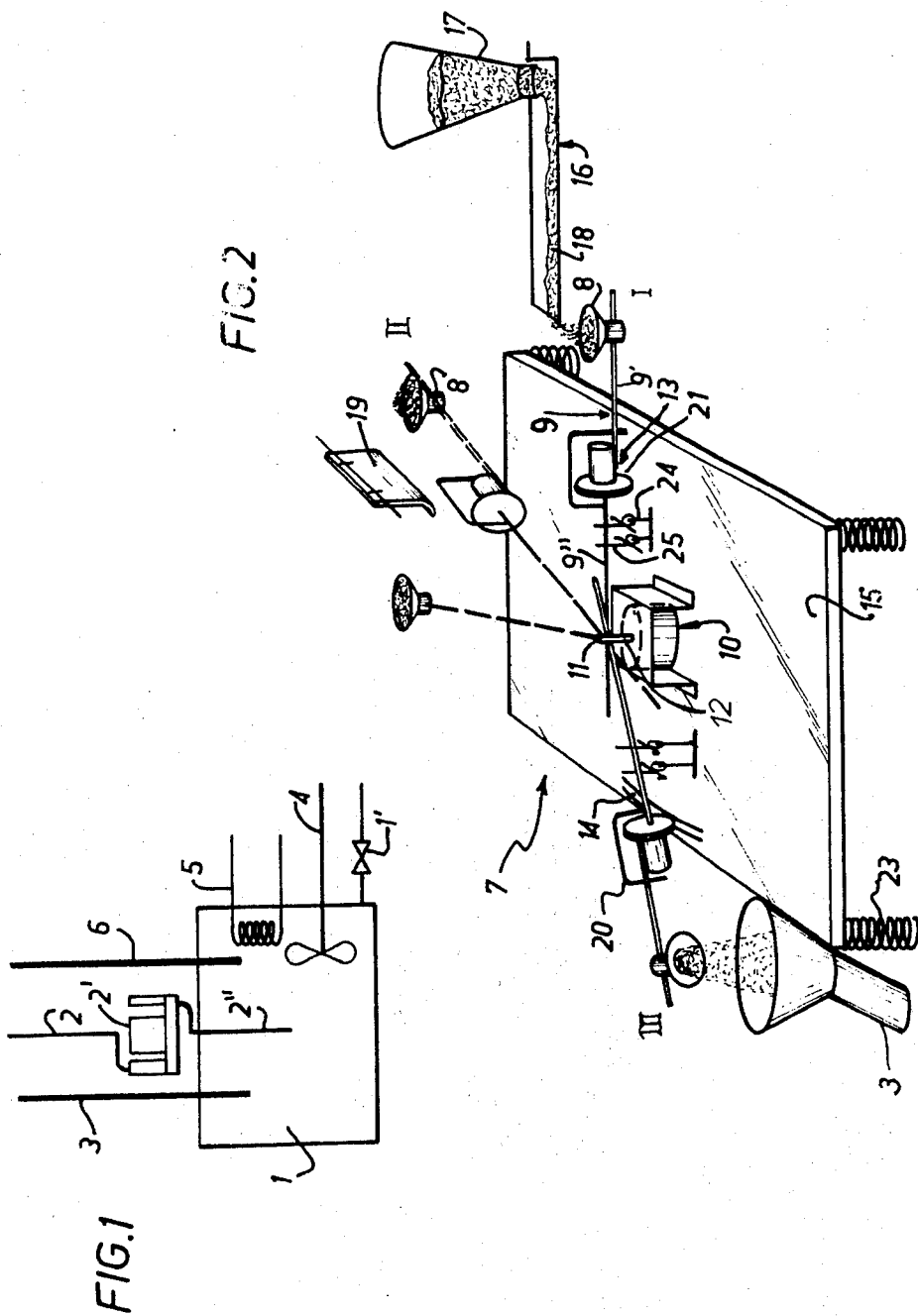


FIG. 3

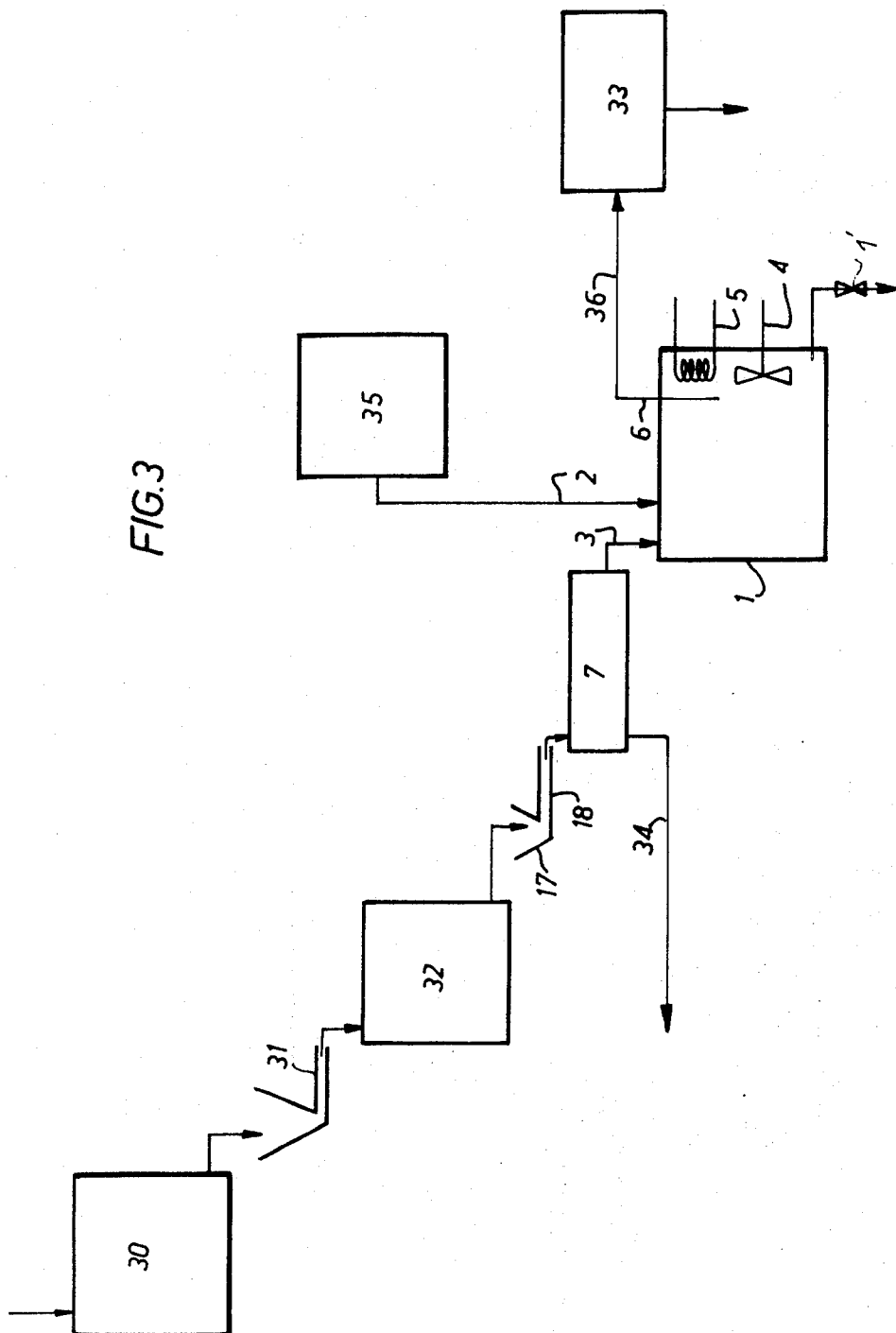
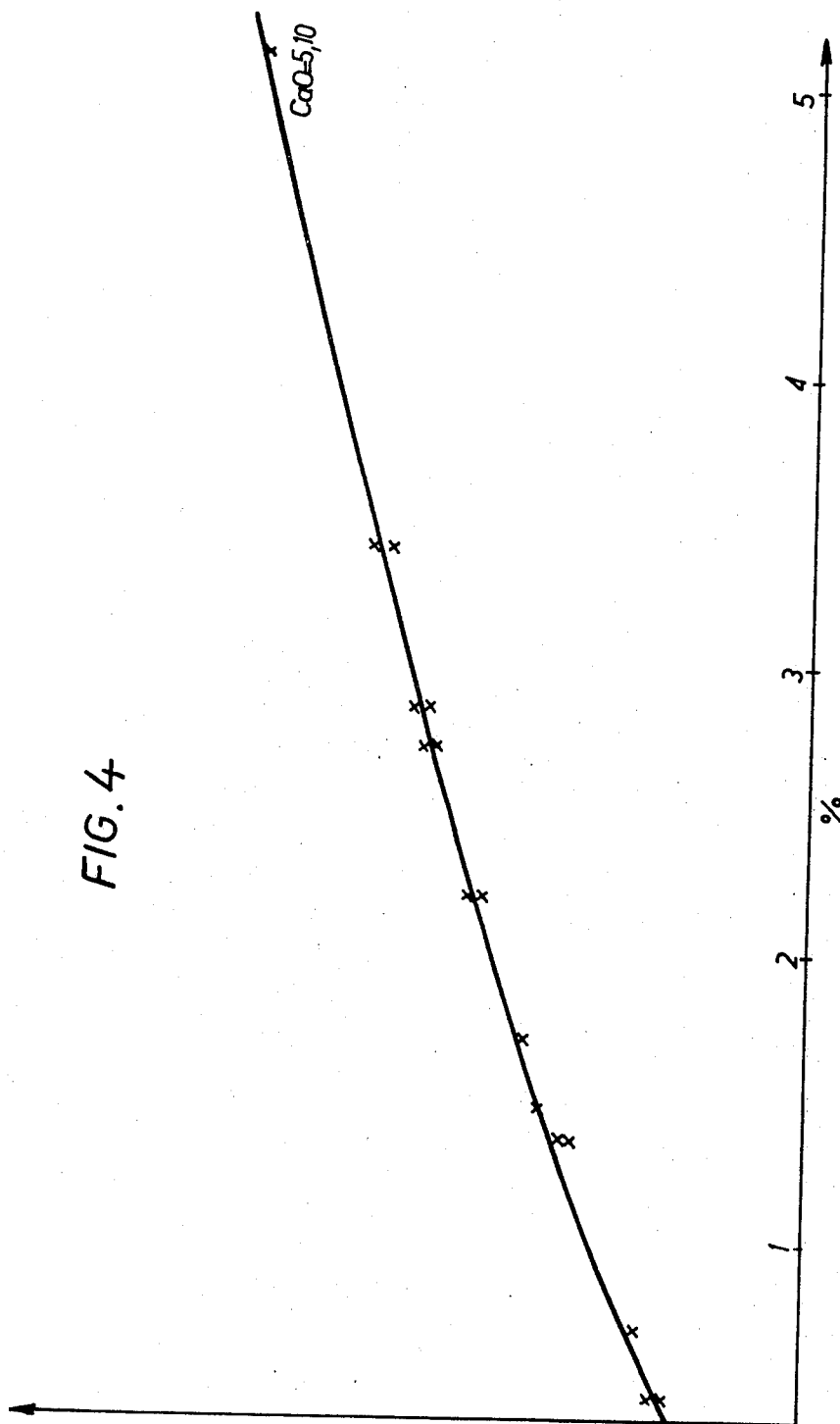


FIG. 4



PROCESS AND DEVICE FOR THE QUANTITATIVE ANALYSIS OF FREE LIME

This invention concerns an improved process for quantitative analysis of the free lime content of cement. It also concerns an improved analysis device, particularly suitable for the quantitative analysis of free lime in cement, and a unit for the automatic control of a cement kiln including such a device.

Quantitative analysis of lime involves measuring out a given quantity of the powder to be analysed and mixing it with a reagent, followed by actual analysis, usually by colorimetric methods.

Previously, lime was measured intermittently, which meant that it could not be used for continuous regulation of a kiln. Continuous analysis involved extremely fragile, expensive appliances, such as X-ray diffraction measurement instruments, continuous balances and other devices, which cannot be fitted to production units like cement kilns, for reasons of cost and fragility.

Quantitative analysis of the free lime content of a material such as cement clinker can be used in calculating the burning rate for an unfired material; in addition, automatic operation of a cement kiln can be regulated on the basis of the quantity of free lime in the clinker from the kiln. In fact, this has not previously been possible, since the clinker is not available until it has left the cooler, approximately half an hour after actual burning, further increasing the time needed to obtain the results of analyses, so that the free lime content of the clinker cannot be found quickly enough for kiln-regulation purposes.

This invention overcomes the drawbacks of existing methods, offering a method of almost continuous analysis of free lime content, and allowing kiln-operating variables to be selected and balanced more efficiently.

Quantitative analysis of the free lime content is useful not only in automated kiln operation, but also as a way of improving the quality and uniformity of clinker, and consequently cement. This invention provides manufacturers with an inexpensive, compact appliance to analyse the lime content, considerably facilitating the use of lime-measurement methods for industrial purposes.

The invention concerns a process for the quantitative analysis of the free lime content of a sample of powder, in which a given quantity of the powder is mixed with a given quantity of reagent in a container, characterized by the fact that analysis is done in this container, and consists of conductimetric, potentiometric, pH-metric or similar methods, the said container being heat-regulated if necessary.

According to one feature of the invention, the given quantity of powder fed into the container is of uniform grading.

According to another feature, this quantity of powder of uniform grading is obtained by measuring out a uniform volume.

According to another feature of the invention, this uniform volume is obtained by pouring the powder loose into a calibrated receptacle vibrating it so that it will settle, and levelling it off.

In one embodiment of the invention, a calibrated receptacle moves round a circular path, in the course of which it passes through a filling zone, a levelling-off zone and an emptying zone, while compression occurs

along at least one part of the path between the filling zone and levelling-off zone.

The invention also concerns a device comprising a container, means of measuring out and conveying separate given quantities of reagent to this container, means of feeding the sample to be analysed into the container, means of stirring the contents of the container, and a heat-regulation system for the container, and also comprising means for the actual quantitative analysis, including an electrode for potentiometric, conductimetric, pH-metric or similar analyses, and means of emptying the container at regular intervals. The electrode is preferably connected to an electronic processing unit, which emits a signal intended for a computer and/or recording device.

In one embodiment of the invention, the appliance to measure out a given volume of powder with uniform grading comprises a calibrated receptacle fixed on an arm connected to a motor which moves it in an approximately horizontal direction, a joint allowing the part of the arm to which the receptacle is attached to rotate on its longitudinal axis, upturning the receptacle, means of producing rotation of this part of the arm, means of returning the arm to the position in which the receptacle is filled, and means of causing vibration of the receptacle during at least part of its approximately horizontal movement.

According to one feature of the invention, this appliance to measure out a given volume of powder includes a power-feed system, and a device for levelling off the surface of the powder in the receptacle.

The joint allowing the part of the arm to which the receptacle is attached to rotate is preferably located between the motor and the receptacle.

In one embodiment of the invention, the means of producing rotation of the part of the arm to which the receptacle is attached consist of a device operating on the joint.

According to another feature of the invention, the motor is attached to a base plate, to which the device operating on the joint is attached, and which includes means of causing vibration of the receptacle.

According to yet another feature, the means of returning the arm to the position in which the receptacle is filled consist of a spring.

Vibration is preferably provided by a separate vibrator, operating either on the base or directly on the arm to which the receptacle is attached.

The invention also concerns the use of this device in a unit for the automatic operation of a cement kiln, comprising means of grinding to a given grain-size, means of measuring out a given quantity of the powder to be analysed, means of feeding this sample into a container in which it is mixed with a given quantity of reagent, and means of quantitative analysis in this container, connected with a device emitting a signal to a computer and/or logic analyser.

In one embodiment of the invention, this device is controlled by a measurement signal emitted by the quantitative analysis instrument and by a logical signal reflecting the measurement, emitted by a device connected with the mixing container.

Other aims and advantages of the invention are shown in the following description, with reference to the accompanying drawings. The invention is of course not confined to this embodiment.

FIG. 1 shows an improved quantitative analysis container, as proposed in the invention.

FIG. 2 shows an appliance to measure out a sample of a given volume of powder, as proposed in the invention.

FIG. 3 shows an automatic kiln-control unit, as proposed in the invention.

FIG. 4 shows the output in volts of the conductimeter, corresponding to the free lime content.

FIG. 1 shows a container for the quantitative analysis of the free lime content of a sample of powder.

This container 1 comprises means 2 of conveying at least one given quantity of reagent, measured out by a device 2'.

This device 2' may consist of a revolving plate containing calibrated receptacles which pass in turn in front of a filling chute 2 and a pipe 2'' conveying the reagent to the container.

The sample of powder to be analysed is fed into the container through a funnel 3.

The container includes means of stirring the contents, consisting of a standard agitator 4, and means of regulating the temperature of the container, consisting of a spiral pipe 5 inside which circulates a heating or cooling fluid, or an electric heating system. This container also includes an emptying device 1', which operates at given intervals.

One end of the electrode 6 is submerged in the container 1. This electrode consists of a conductimetric, potentiometric, pH-metric or similar electrode, connected to an electronic processing unit which delivers a signal sent to a recording device and/or analogue computer.

The improvement proposed by this invention consists of performing quantitative analysis in the same container in which the given quantity of the agent and the sample are mixed, and ensuring simultaneous arrival, at regular intervals, of these quantities of reagent and powder, as well as automatic regular emptying of the container.

The container may be combined with an appliance 7 to measure out a given volume of powder of uniform grading, as shown in FIG. 2.

This appliance comprises a calibrated receptacle 8, fixed on an arm 9 connected to a motor 10 which drives it, thereby moving the receptacle in an approximately horizontal direction, around a circumference centred on the point 11, at which the arm 9 is attached to the vertical axle 12 of the motor 10.

There is a joint 13 on the arm 9, allowing part 9' of the arm 9 to rotate on its longitudinal axis, this rotation being produced by a flange 14, or similar device such as a pin. The arm also has a device to ensure that it returns the receptacle 8 to its original position, such as a spring (not shown here).

The appliance 7 includes means of causing vibration of the receptacle during part of its approximately horizontal movement. This may consist of a vibrating plate 15 operated by a separate motor (not shown here). The appliance also includes a powder-feed system 16, consisting of a hopper 17 and chute 18, which can also vibrate, and the width of which corresponds to the length of the filling zone for the receptacle. A scraper 19 levels off the surface of the contents of the receptacle.

The appliance operates as follows.

The arm 9 is driven by the motor 12, so that the receptacle 8 moves along a circular path, into a filling

zone (position I), where the crushed clinker from the hopper 17 is poured into it. The filling zone is the same width as the chute 18, and the receptacle 8 is filled as it moves under the chute. Simultaneously, its contents are compressed by the vibrations imparted to the arm 9. It then moves on until it reaches position II, where the surface of the contents is levelled off by a scraper 19.

The receptacle continues to position III, where a flange 14 operates the joint 13, upturning the receptacle and transferring the contents into a discharge funnel 3 (which feeds the container 1 in FIG. 2). A stop 20, level with the joint 13, limits rotation of the receptacle. The joint preferably consists of a toothed wheel 21, which rotates when it comes into contact with the flange 14, upturning the receptacle 8.

The receptacle continues along its circular path, and when the toothed wheel 21 moves away from the flange 14, a spring returns the arm and receptacle to the filling position. The receptacle continues until it reaches position I as before.

This appliance allows a given quantity of powder to be measured out, provided that the powder has uniform grading. Compression and levelling-off help to ensure a given volume.

The system for causing the receptacle 8 to vibrate can consist of a vibrating plate 15, on springs 23, driven by a separate motor, or a device connected to the arm and to the plate 15, consisting of a microswitch 24 and cam 25 on the arm. This unit is connected electrically to a Sinex vibrator screwed beneath the plate 15.

The unit shown in FIG. 2, which can be fitted to the kiln cooling outlet, comprises a jaw-breaker 30, vibrating chute 31, and continuous crusher 32, designed to produce samples with uniform grading, with a Blaine specific surface-area of approximately 3,500 sq.cm/g. The continuous crusher 32 is connected to the appliance 7 to measure out a given volume of powder.

At regular intervals, the appliance 7 tips a fixed volume of powder through a funnel 3 into a container 1, in which there is an electrode 6. A fixed quantity of reagent is also conveyed at regular intervals from a reagent tank 35 into the container, through a funnel 2. This appliance is connected to an electronic unit which emits a logical signal conveying the measurement to a computer, and is combined with a device to record the results obtained by conductimetric, pH-metric, potentiometric, or other analytical techniques, and a unit to emit a second signal in the direction of a computer, which controls the kiln-regulating system to which the unit in FIG. 2 is attached.

This unit provides almost uninterrupted quantitative continuous analysis of the free lime content of clinker, and allows kiln-operating variables to be controlled and balanced.

The jaw-breaker 30 is preferably a Minemet-type crusher, preferably giving a grain-size of between 0 and 4 mm. It is connected to a sampler (not shown here), beneath the clinker belt in the clinker unit (not shown here). The sample is 2 to 3 litres/hr for an hourly output of 60 tons of clinker.

The continuous crusher 32 may be a vibrating crusher, which has to be fed continuously, to ensure the required degree of fineness. The vibrating chute 31 is preferably a vibrating hopper, but may be of any other type, such as an overflow device, providing a continuous supply.

The appliance 7 allows a fixed volume of the powder supplied by the vibrating hopper 17 to be measured out.

The unit formed by the appliance 7 and container 1 operates as follows.

The motor 10 is a reducing motor (1 revolution every 3 minutes, for instance), which drives the arm 9 so that the receptacle 8 passes beneath the jet of powder from the vibrating chute 18. The receptacle is filled to its capacity of approximately 1 cc, and continues its circular movement. The device formed by a cam on the arm and a microswitch on the plate 15 causes vibration of the arm and receptacle, compressing the powder inside the receptacle uniformly, so that a uniform weight is obtained by volumetric measurement. Any excess is removed by this vibration, and the receptacle then passes under a scraper 19, which levels off the powder at the edges. Any powder remaining on the arm is removed by conventional means.

When the receptacle 8 reaches the emptying position, the joint, which consists of a toothed wheel 21, comes into contact with the flange 14, and completes a 180° movement, causing the part 9' of the arm 9 to rotate on its longitudinal axis. A device similar to the one used during the filling phase, consisting of a cam and microswitch, can be used here to vibrate the receptacle 8 in its upturned position, to ensure complete emptying. The arm then comes to rest in an intermediate position, and the starting signal for a new weighing cycle comes from the analysis container 1.

The powder is conveyed into the container 1 through the funnel 3, into which the receptacle 8 has been emptied. The samples of powder may consist of 1 g of clinker, fed into the container every 15 minutes. Simultaneously, 100 ml of glycol are conveyed to the container from a tank 35. The solution is stirred in the container 1 by an agitator 4.

The temperature of the solution in the container 1 should be regulated to within 0.5° during analysis, by means of a thermometer and heating tube 5. The conductimetric electrode 6 consists of a probe, the base of the protective glass casing of which is removed, to prevent cement powder from accumulating inside the electrode. A thermometer (not shown here), connected to a conductimeter 33, is used to adjust results to allow for residual fluctuation in the temperature of the solution. The signal from the conductimeter cell connected with the electrode 6 is sent to an electronic processing unit, which delivers a signal to an analogue computer and/or recording appliance (not shown here).

The appliance shown in FIG. 1 is extremely accurate, as the test results given below show, for two different crushing operations: the weight obtained by volumetric measurement, using the appliance 7, is found to be uniform.

	1st crushing	2nd crushing
1st measurement	0.99 g	1.035 g
2nd measurement	0.99	1.05
etc.	0.99	1.01
	0.98	1.00
	0.98	0.995
	0.97	0.99
	0.98	0.99
	0.97	0.99
	0.99	0.99
	0.99	
	0.98	

-Continued

	1st crushing	2nd crushing
5	0.98	
	0.98	

The quantity of lime in a clinker is measured using the appliance shown in FIG. 1, set to perform four analyses hourly. The graph in FIG. 4 shows the results of the output in volts of the conductimeter, corresponding to the free lime content, measured by the complexometric method. The electric signal is found to be quite suitable for use.

Reproducibility measurements carried out for one clinker and one crushing operation produce an output-voltage variation of 0.1 volts, i.e. a variation of 0.1 % in free lime content.

A standard variation of 0.15 can be obtained for the measurement of free lime. Automatic analysis is slightly less accurate than the complexometric method, carried out by an experienced operator, where the normal variation is 0.1. It is quite adequate, however, for automatic kiln operation. In addition, the frequency of measurements allows the output signal to be filtered slightly.

Naturally, the invention is in no way confined in the embodiments described here: many alternative forms are possible, for someone skilled in the art, and depending on the application involved, without any departure from the spirit of the invention.

What is claimed is:

1. A method of controlling at least one operating parameter of a kiln adapted to subject a product containing free lime to a heat treatment, comprising the steps of:

crushing the heat treated product issuing from the kiln to obtain a powdrous substance; sampling at substantially regular time intervals successive amounts of said powdrous substance, said sampling step being carried out by filling at said substantially regular intervals of time a calibrated receptacle with said powdrous substance so as to obtain therein successive measured amounts of said substance;

introducing said measured amounts successively into a container while simultaneously introducing into the latter measured amounts of a reagent adapted to allow the free lime content of said powdrous substance to be determined by analysis;

quantitatively analyzing the mixture of powdrous substance and reagent thus obtained in said container so as to determine the free lime content of said powdrous substance in said container;

producing a signal representing the free lime content thus determined; and

transmitting said signal to an appliance associated to said kiln and adapted to determine said at least one operating parameter of said kiln in response to said signal.

2. The method of claim 1, wherein the successive measured amounts of powdrous substance have a substantially uniform granulometric grading.

3. The method of claim 1, wherein the analysis is effected by a conductrimetric, potentiometric or pH-metric analyzing process.

4. The method of claim 1, wherein said receptacle is submitted to vibration, at least during the introduction of said successive amounts of powdrous substance into said receptacle.

5. The method of claim 1, wherein each one of said successive amounts of powdrous substance introduced into said calibrated receptacle is greater than the measured amount as determined by the calibration of said receptacle, and wherein the excess of powdrous substance thus introduced into the receptacle is removed prior to introducing the measured amount of powdrous substance thus obtained into said container.

6. The method of claim 1, wherein said receptacle is moved continuously along a substantially horizontal circular path comprising a filling location at which said powdrous substance is introduced into said receptacle and a discharge station at which said powdrous substance is transferred from said receptacle into said container.

7. A device for controlling at least one operating parameter of a kiln adapted to subject a product containing free lime to a heat treatment the heat treated-product issuing from said kiln, said device comprising:

means for crushing said product;
a container;

means for successively measuring at substantially regular intervals of time samples of the crushed heat-treated product issuing from said crushing means and for introducing said samples into said container;

means for successively feeding at substantially regular intervals of time measured amounts of a reagent into said container;

means for quantitatively analyzing within said container with the aid of said reagent the free lime content of the samples introduced into said container;

means for sensing the result of the quantitative analysis and for producing a signal representing said free lime content;

means for controlling said kiln operating parameter in response to said signal; and

means for transmitting said signal from said signal producing means to said control means.

8. A device for controlling at least one operating parameter of a kiln adapted to subject a product containing free lime to a heat treatment, comprising:

a crusher for crushing the heat-treated product, a calibrated receptacle movable between a filling location wherein it is filled with an amount of the crushed product and a discharging locating

wherein said amount of product is introduced into a container;

means for displacing at regular intervals of time said receptacle between said filling and discharging locations;

means for introducing measured amounts of a reagent into said container;

means for quantitatively analyzing the mixture of said crushed product and said reagent thus obtained in the container for determining the free lime content of said crushed product;

means for producing a signal representing the free lime content determined by said analyzing means;

means for controlling said kiln operating parameter in response to said signals; and

means for transmitting the latter from said signal producing means to said control means.

9. The device of claim 8, wherein said receptacle has an open end and is mounted on a first portion of a substantially horizontal arm, a second portion of which is rotatably mounted on a substantially vertical motor-driven axis, said first and second arm portions being interconnected by a rotary joint adapted to bring selectively said first arm portion into a first position wherein the open end of the receptacle mounted therein is in an upright position with its open end directed upwardly, and into a second position wherein said receptacle is in an inverted position with its open end directed downwardly, means being provided for bringing said first arm portion into said first position while said arm moves said receptacle to said filling location and from the latter to said discharging location, and for bringing said first arm portion into said second position when said arm has moved said receptacle to said discharging location.

10. The device of claim 9, wherein said receptacle open end has a planar peripheral rim, and wherein scraper-like means are provided on the path of said receptacle along which the latter moves from said filling location to said discharging location, said scraper-like means being adapted to level off the surface of the product contained in the receptacle by scraping away any excess amount of said product which may protrude over said planar rim.

11. The device of claim 9, wherein vibrating means are provided for vibrating said receptacle.

12. The device of claim 9, wherein stirring means and temperature regulating means are arranged in said container.

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