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A Rapid Method for Determining Compound Composition of Cement Clinker: Application to Closed Loop Kiln Control

Abstract: A procedure for determination of phase composition of commercial cement clinker using quantitative x-ray powder diffraction analysis is described. An external standard and comparison of peak heights rather than the peak areas are used for rapid analysis. Several standard curves were prepared using diffraction patterns from known mixtures of previously prepared pure components which exist in cement clinker. For purposes of comparison, both the suggested external standard method and the internal standard method which is generally accepted for quantitative X-ray diffraction analysis were used. It was found that the faster external standard method gives analysis of important clinker constituents with accuracy adequate for quality control in a cement plant. With the use of suggested grinding procedure and an automatic sample changer attachment to standard X-ray diffraction equipment, it is possible to obtain an on-line analysis of clinker in one half hour. This analysis can then be deployed in performing closed loop control of a cement kiln with a proposed algorithm.

Introduction

The properties of cement are influenced by its compound composition, that is, by the relative proportions of its chemical constituents; however, no direct method for determining compound composition is in use by commercial cement manufacturers at present. Rather, an indirect procedure is followed in which the product is subjected to chemical analysis and compound composition is computed from the analysis under the assumption of equilibrium reaction conditions.

A problem that has plagued the cement industry is the absence of a rapid method for chemical analysis of the final product from the kiln—commonly known as clinker. Conventional gravimetric methods for complete chemical analysis of clinker require approximately 24 hours to test the clinker quality. Because of the high production rate of a kiln, and because of the indirect procedure for determining compound composition, which frequently yields erroneous results,[1] considerable loss in production or deterioration of product quality may occur during the time required for analysis. While several attempts[2–5] have been made to use x-ray diffraction analysis for directly ascertaining the compound composition of cement clinker, the procedures employed by previous workers have been more or less useful only as research tools due to the long time (5–12 hours) required for analysis.

In this paper, an x-ray diffraction procedure is described for analysis of those cement compounds which significantly affect product quality. Using this procedure in combination with proposed methods for sample preparation and grinding and with the use of an automatic sample changer, it should be possible to accomplish the desired analysis in about one-half hour. Since the processing time for material in the kiln is of the order of 5 hours, the procedure offers the possibility of on-line computer control of product quality.

Scope of investigation

Present attempts to improve the performance of a cement kiln through the use of digital and analog computers rely mainly on:

(1) Optimum blending of the raw materials using elemental analysis of quarry materials by x-ray fluorescence.

(2) Control of burning-zone temperature in the kiln.

(3) Prediction of ring formation and other phenomena which cause shutdowns so that proper corrective actions based on operator experience may be taken.

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(4) Attempts to minimize the effects of such external disturbances as varying ambient conditions and inconsistent fuel quality.

Because the performance of a cement kiln is dependent on so many parameters, any one or all of these steps will not *assure* uniform clinker quality, even through it may significantly improve kiln performance. For example, Step 1 provides only elemental analysis, and if the crystalline nature of SiO_2 in raw material changes from clay to quartz, the burnability of clinker is drastically changed, and even with control of burning zone temperature, the clinker quality may be seriously affected. An analytical tool which can provide product quality information rapidly can be of invaluable assistance in kiln control. This information can be used as feedback control on several directly or indirectly controllable variables (such as burning zone temperature, kiln speed, raw material blending, etc.).

As far as on-line control is concerned, the analytical procedure for determining product composition need not be accurate in the sense of measuring exact composition. One is interested only in an accurate assessment of the relative shift in weight fraction of one, two, or more compounds. For example, an increase in dicalcium silicate,* either sudden or gradual, over a period of several hours, may be an indication of lower burning zone temperature due to an increase in feed rate to the burning zone, a decrease in fuel rate and/or calorific value of the fuel, an incorrect ratio of limestone to silica, or one of several other factors. Once the increase in C_2S is detected, a computer program may be used to identify those variables which could cause the increase and corrective action may be taken to change the control variables by an amount proportional to the percent variation of C_2S from its normal operating value.

It is not the purpose of this paper to give an accurate relationship between change in cement composition and the operating variables of a cement kiln, the subject being extremely complex as indicated by the literature.[7-9] Rather, it is intended to report a rapid analytical technique that is regarded as a step toward the goal of closed-loop quality control of cement clinker composition with the assistance of an x-ray diffraction technique that yields phase composition rapidly. In the following sections, the theory of quantitive x-ray powder diffraction analysis and the proposed experimental procedure are described. The final section presents a discussion of results and illustrates how one can use this analytical tool for closed-loop control of a cement kiln.

* The notation of cement chemistry will be used hereafter; in it,

$C_3S = 3\ CaO \cdot SiO_2$;
$C_2S = 2\ CaO \cdot SiO_2$;
$C_3A = 3\ CaO \cdot Al_2O_3$;
$C_4AF = 4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

Theory

When a sample consisting of several compounds is subjected to x-ray powder diffraction, the quantitative determination of any compound, i, in the sample is theoretically possible by the application of the following relationship, which is the basic equation for Quantitative X-ray Diffraction Analysis[6] (QXDA).

$$X_i = \frac{I_i \mu_m}{I_i^0 \mu_i}, \tag{1}$$

where

X_i = Proportion by weight of compound i in the mixture.
I_i = Intensity of a selected diffraction peak due to compound i in the mixture.
I_i^0 = Intensity of the selected diffraction peak due to compound i when a pure specimen of compound i is x-rayed under identical test conditions.
μ_m = Mass absorption coefficient of the mixture.
μ_i = Mass absorption coefficient due to compound i alone.

It is obvious from Eq. (1) that if μ_m and μ_i are not significantly different, the quantitative determination of compound composition could be achieved by direct comparison of peak intensities, I_i and I_i^0:

$$X_i = \frac{I_i}{I_i^0}. \tag{2}$$

If the mass absorption coefficient of a compound is significantly different from the mass absorption coefficient of the mixture of which it is a constituent, the frequently used procedure for QXDA consists of intergrinding a known proportion, X_S, of internal standard* with the sample and determination of the unknown, X_i, by applying the following relationship:

$$\frac{X_i}{X_S} = \frac{I_i I_S^0 \mu_S}{I_S I_i^0 \mu_i} = K \frac{I_i}{I_S}, \tag{3}$$

where

I_S = Intensity of the internal standard peak in the mixture.
I_S^0 = Intensity of the internal standard peak when a pure specimen of the internal standard is x-rayed under identical test conditions.
μ_S = Mass absorption coefficient due to the internal standard.
K = A constant which can be evaluated from the samples containing known amount of X_i.

Eq. (3) presents a method whereby differences between the mass absorption coefficient of a compound and the

* Any inert material, with a strong peak in the vicinity of peaks selected for QXDA of compounds in the mixture, and with no overlapping of the internal standard peak by other peaks, can be used as internal standard.

mixture containing it do not affect the results of QXDA because determination of properties of X_i in the sample is possible by direct comparison of the peak intensities of the compound and the internal standard.

The application of the internal standard method to QXDA of compounds in portland cement has been reported by several investigators, including Kantro et al,[2] Smolczyk,[3] Midgley et al,[4] and Berger et al.[5] The method involves precisely weighing predetermined amounts of the sample and the internal standard, intergrinding them in the presence of a dispersing fluid for 2–3 hours, drying the specimen by vacuum and heat treatment (1–2 hrs), subjecting the powder to x-ray analysis and, finally, determining the peak intensities by measuring area under the peaks with a planimeter.* It is obvious that the procedure described above is not amenable to on-line analysis of portland cement clinker, especially due to the long time required for the sample preparation.

Eq. (1), however, can be modified as follows:

$$X_i = \frac{I_i \mu_m}{I_i^0 \mu_i}$$

or

$$\frac{X_i}{\mu_m} = \frac{I_i}{I_i^0 \mu_i} = \frac{I_i I_S^0}{I_S^0 I_i^0 \mu_i} = K \frac{I_i}{I_S^0}, \quad (4)$$

where I_S^0 can be made constant by using an external standard which assures that the test conditions for x-ray diffraction of the sample remain identical to those used for determination of K from a series of standard samples having known amounts of X_i. Equation (4) then reduces to:

$$\frac{X_i}{\mu_m} = K I_i. \quad (5)$$

Furthermore, if μ_m does not change appreciably for a series of samples consisting of varying proportions of a number of compounds, then:

$$X_i = K I_i. \quad (6)$$

Equation (6) suggests that an easy way to perform on-line analysis of cement compounds is by direct comparison of peak intensities obtained by x-ray diffraction of clinker specimens from the rotary kiln.

C_3S (tricalcium silicate) and C_2S (dicalcium silicate) constitute about 80 percent of normal portland cement clinker. As the mass absorption coefficient of C_3S is 102, and that of C_2S is 95, it is expected that minor variations in their amounts would not influence the mass absorption coefficient of clinker. The mass absorption coefficient of C_3A (tricalcium aluminate), which may constitute 5–15 percent of normal portland cement, is 91, whereas, the mass absorption coefficient of the ferrite phase, which usually constitutes 7–10 percent of normal portland cement, and the chemical composition of which approximates the formula C_4AF, is about 140. As the mass absorption coefficient of the ferrite phase is significantly different from the other major constituents of portland cement clinker, it is obvious that variations in the ferrite phase content of clinker affect the validity of Eq. (6), which is based on the assumption that the mass absorption of samples containing different proportions of certain compounds remains fairly constant.

On the theoretical considerations, therefore, it is obvious that while the internal standard technique is more accurate, the external standard technique appears to be rapid and readily adaptable to on-line analysis. In this investigation we have used both the internal and external standard techniques to prepare standard curves with the purpose of showing that for on-line analysis the more rapid external standard method gives adequate comparison.

Experimental procedure

In order to obtain the standard specimens of portland cement clinker, the individual constituent compounds, C_3S, C_2S, C_3A, and C_4AF, were made separately and then blended in required proportions. In this manner, specimens containing a wide range of known compound compositions were prepared. Details of procedures on the preparation of compounds, preparation of standard specimens and their QXDA will be now discussed.

- *Preparation of pure compounds*

The preparation of pure compounds was carried out at the facilities of the Engineering Materials Laboratory of the University of California, Berkeley. Stoichiometric preparations of analytical-reagent-grade calcium carbonate, silicic acid, aluminum hydroxide and iron oxide were used to prepare raw mixes for making the pure compounds. Each raw mix was ground in a pebble mill, made into a paste with distilled water, and dried to disk-shaped cakes which were heat-treated repeatedly in a furnace until no impurities in the desired compound were detectable by x-ray diffraction.

In the case of C_3S, small amounts of magnesium oxide were added to the raw mix so that the chemical analysis of the final product showed one percent MgO and one percent Al_2O_3. This served to stabilize the C_3S in monoclinic form, which is the usual form of C_3S* in commercial portland cements. In the case of C_2S, the commercial cements normally contain the beta form of C_2S. About one percent

* Berger, et al.[5] use a digital data collection system and a computer to analyze the results recorded on punched paper tape.

* C_3S so substituted is called alite, but for the purpose of maintaining uniform nomenclature, the given formula is used.

CaO was used as a stabilizer for beta C_2S. In addition, quick cooling of the product was required in order to prevent its conversion to gamma C_2S. No special problems were encountered in the preparation of C_3A and the ferrite phase.

• *Preparation of standard specimens*

Commercial portland cement clinker may contain 30–70 percent C_3S, 10–50 percent C_2S, 0–15 percent C_3A and 5–20 percent** ferrite phase, C_4AF. Normally, the calcium silicates amount to about 80 percent, whereas, the remaining 20 percent of clinker is constituted of the tricalcium aluminate and the ferrite phase. Table 1 shows the data on twenty standard specimens which were correspondingly designed to cover a broad range of compound compositions. The pure compounds, ground to pass 200-mesh sieve, were proportioned in accordance with the plan shown in Table 1. The mixes were contained in air-tight plastic vials and were blended together thoroughly by a mechanical blending device.

• *Selections of peaks for QXDA*

Table 2 shows the peaks which have been selected for quantitative representation of the various compounds. Kantro et al[2] use 41.0° 2θ and 51.8° 2θ peaks in conjunction with a set of mathematical equations for determination of C_3S and C_2S content in cement. They state that their choice of these peaks is governed by the consideration that the diffraction pattern of C_3S does not contain any strong peaks which are not overlapped by C_2S peaks and vice versa. On the other hand, other investigators, including Smolczyk[3] and Midgley,[4] believe that 30.1° 2θ and 51.8° 2θ peaks in C_3S pattern are not overlapped by any C_2S peak and are adequate for quantitative determination of C_3S. Similarly, the 31.1° peak in the clinker pattern is due solely to beta C_2S and the 33.2° and 33.8° peaks are due solely to C_3A and C_4AF, respectively.

• *Equipment for x-ray diffraction analysis*

The equipment used for x-ray diffraction analyses consisted of an x-ray generator having a Cu target and a Ni filter, a diffractometer coupled with a scintillation counter, and an *x-y* recorder. This is a standard type of equipment available in x-ray analytical laboratories. The samples were x-rayed under the following conditions:

Voltage = 40 kV
Current = 35 mA
Receiving slit = 0.0006 in
Base line = 9 V
Pulse height = 19.8 V
Time constant = 4.

** Except white cement which, being low in Fe_2O_3, has a very small amount of ferrite phase.

Table 1 Compound composition of standard clinker samples

Sample	C_3S	C_2S	C_3A	C_4AF
Ia	30%	50%	10%	10%
Ib	30	50	5	15
Ic	30	50	0	20
Id	30	50	15	5
IIa	40	40	10	10
IIb	40	40	5	15
IIc	40	40	0	20
IId	40	40	15	5
IIIa	50	30	10	10
IIIb	50	30	5	15
IIIc	50	30	0	20
IIId	50	30	15	5
IVa	60	20	10	10
IVb	60	20	5	15
IVc	60	20	0	20
IVd	60	20	15	5
Va	70	10	10	10
Vb	70	10	5	15
Vc	70	10	0	20
Vd	70	10	15	5

Table 2 Peaks selected for QXDA analysis

Compound	*Degrees* 2θ (Cu, Ka)	*d*, Å
C_3S	30.1	2.97
beta C_2S	31.1	2.87
C_3A	33.2	2.70
C_4AF	33.8	2.65
background	30.5	2.93

Theoretically, the peak intensities are better represented by peak areas rather than by peak heights, so in the internal standard method, step counting at 0.02 degrees 2θ at 3,200 counts per second was adopted.

From the analysis of diffraction patterns it was, however, established that considerable overlapping between the peaks made the determination of area under a particular peak difficult. Hence, practical considerations of on-line cement analysis made peak-height measurement the preferred method for representing peak intensities. Measurement of peak heights made it possible to use the faster procedure (external standard method) which involved scanning the specimens in 29–34 degrees 2θ range at 1/4 degree 2θ per minute and 100 counts per second counting rate. A silicon disk was used as the external standard.

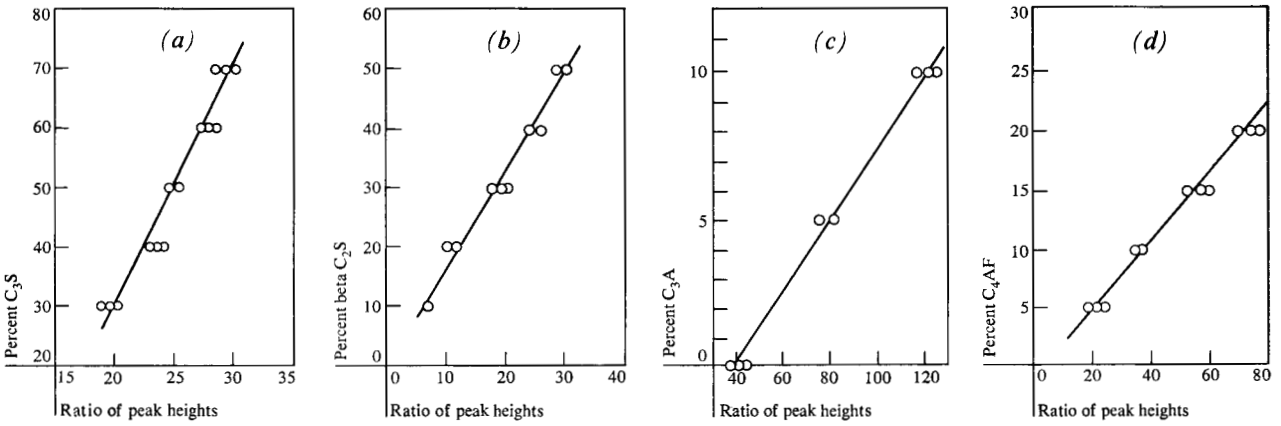
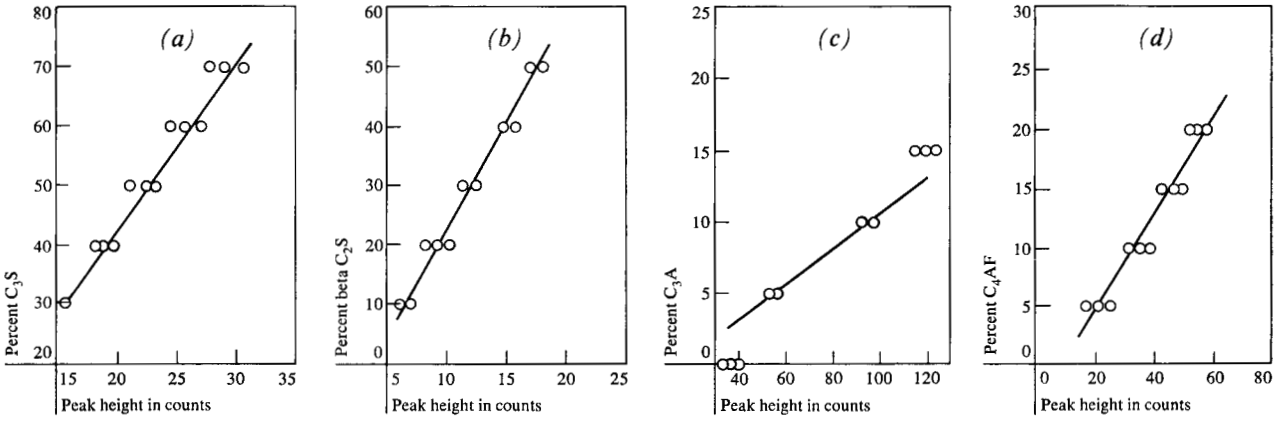


Figure 1 Calibration curves for internal standard method. Internal standard is the 36.1° peak of TiO_2. Computed ratios compare heights of (a) 30.1° C_3S peak, (b) 31.1° C_2S peak, (c) 33.2° C_3A peak, (d) 33.8° C_4AF peak, to that standard.

Figure 2 Calibration curves for external standard method. External standard is silicon disk. Direct comparison of peak heights with standard is given for (a) 30.1° C_3S peak, (b) 31.1° C_2S peak, (c) 33.2° C_3A peak, (d) 33.8° C_4AF peak.



• *Preparation of sample for x-ray diffraction analysis*

In the internal standard method, 20 percent TiO_2 was used as internal standard. Two grams of precisely weighed sample of a standard cement and 0.4 grams of precisely weighed TiO_2 were ground for one hour in a mechanical Alundum grinder, using 25 ml of trichloroethylene as a dispersing agent. The ground paste was dried in a vacuum drying oven for about an hour in order to drive off the dispersing agent. In the external standard method, the incorporation of TiO_2 was omitted; hence, no weighing of the standard sample was necessary. In order to obtain a finely ground specimen, however, the same grinding and drying procedure, as used above for internal standard method, was adopted.

In addition to fine grinding, prevention of preferred orientation in the sample is necessary for quantitative x-ray diffraction work. In the present investigation, this was achieved by placing an aluminum sample holder, open at both ends, on top of a clean glass slide, filling the cavity lightly with the sample and sealing off the front opening of the holder with another glass slide fixed to it firmly with transparent tape. The surface of the specimen on the back side of the holder was now ready for exposure to the x-rays. In a few preliminary trials on a standard specimen, reproducible peak heights were obtained, thus assuring a minimum of preferred orientation when the samples were prepared in the above manner.

Results and discussion

Table 3 shows the data on ratio of heights of peaks selected to represent the given compounds quantitatively to the height of the internal standard peak. These data have been used to plot standard calibration curves for C_3S, C_2S, C_3A and C_4AF, which are shown in Figs. 1a, b, c and d

respectively. The samples were x-rayed only once, so that the results could not be rechecked as required by the normal recommended practice for quantitative x-ray diffraction analysis. Hence, about 10 percent of the recorded points, which were abnormal, have been disregarded in the construction of standard curves.

Table 4 shows the data on direct comparison of peak heights by the external standard method. The data is plotted to yield standard calibration curves for C_3S, C_2S, C_3A and C_4AF in Figs. 2a, b, c, and d, respectively.

By comparing the standard curves based on internal standard method with those based on the external standard method, it can be observed that both the methods have yielded comparable straight line calibration curves. Table 4 shows that by the external standard method, good reproducibility of 30.1° C_3S peak and 31.1° C_2S peak is possible,* while fair reproducibility for 33.2° C_3A peak and 33.8° C_4AF peak is obtained. Some of the abnormal values for C_3A and C_4AF phases could perhaps have been rectified if the samples had been x-rayed again to check for the existence of preferred orientation.

Considering that the internal standard method requires precise weighing of both the sample and the internal standard, that it is necessary to intergrind them in a dispersant for 2-3 hours and then to vacuum-dry the slurry for 1-2 hours, and that the x-ray diffraction (step scanning) operational time is about 12 hours per sample, the results obtained with the rapid external standard method appear to be very encouraging. Berger et al[5] have, however, recently developed a fast (one to two hours exclusive of sample preparation time) internal standard procedure of QXDA for routine mineralogical analysis of portland cement in the laboratory. This method utilized a computer to analyze the results recorded on punched paper tape. In the present investigation employing the external standard procedure, the operational period for x-ray diffraction analysis at 1/4° 2θ scanning speed for the required 29–34 degrees 2θ range is only 20 minutes. Although the time spent in the laboratory for fine grinding of samples was about one to two hours, it is possible to reduce it to about two minutes by using a small air-swept grinding mill fed with a sample of clinker drawn from a cement kiln by an automatic sampling device. Weighing of the sample is not required because it is not necessary to use any internal standard, as discussed above.

An automatic sample changer for x-ray diffraction purposes has already been developed.[5] If an automatic sample loading device could be combined with such a sample changer, it should be possible to complete an on-line analysis of clinker compounds from cement kilns within one-half hour.

* Peak heights within each of the major sample groups, i.e., Group I, II, III, IV and V, which contained the same proportion of C_3S and C_2S in a group, have clearly reproduced themselves again and again.

Table 3 Peak height ratios in standard samples using TiO_2 internal standard

Sample No.	30.1°/36.1°	31.1°/36.1°	33.2°/36.1°	33.8°/36.1°
Iay	18	28	107	34
Iby	20	28	92	54
Icy	19	30	49	72
Idy	18	27	182	20
IIay	26	23	130	34
IIby	27	25	103	57
IIcy	28	28*	33*	81*
IIdy	25	23	192	23
IIIay	31	17	119	34
IIIby	35*	19	83	61*
IIIcy	31	17	42	73
IIIdy	29	18	208	21
IVay	32*	10	121	35
IVby	38	11	77	52
IVcy	37	11	44	70
IVdy	36	11	208	22
Vay	41	7	126	37
Vby	43	7	72	43*
Vcy	41	7	57*	72
Vdy	39	7	184	21

* These values are considered abnormal and have, therefore, been disregarded in plotting the calibration curves.

Table 4 Direct comparison of peak heights in standard samples using silicon external standard

Sample No.	30.1°	31.1°	33.2°	33.8°
Ia	16	16	78*	31
Ib	16	17	69*	50
Ic	16	16	36	74*
Id	16	19	140*	23
IIa	19	14	98	30
IIb	21*	15	74*	41
IIc	18	15	37	54
IId	18	15	100*	21
IIIa	24	10	96	58*
IIIb	22	12	54	49
IIIc	22	12	34	57
IIId	22	12	120	17
IVa	28	12*	90	31
IVb	27	9	52	43
IVc	37*	9	20*	55
IVd	26	10	126	10*
Va	30	7	98	36
Vb	31	6	54	36*
Vc	34*	7	26	57
Vd	29	7	114	17

* These values are considered abnormal and have, therefore, been disregarded in plotting the calibration curves.

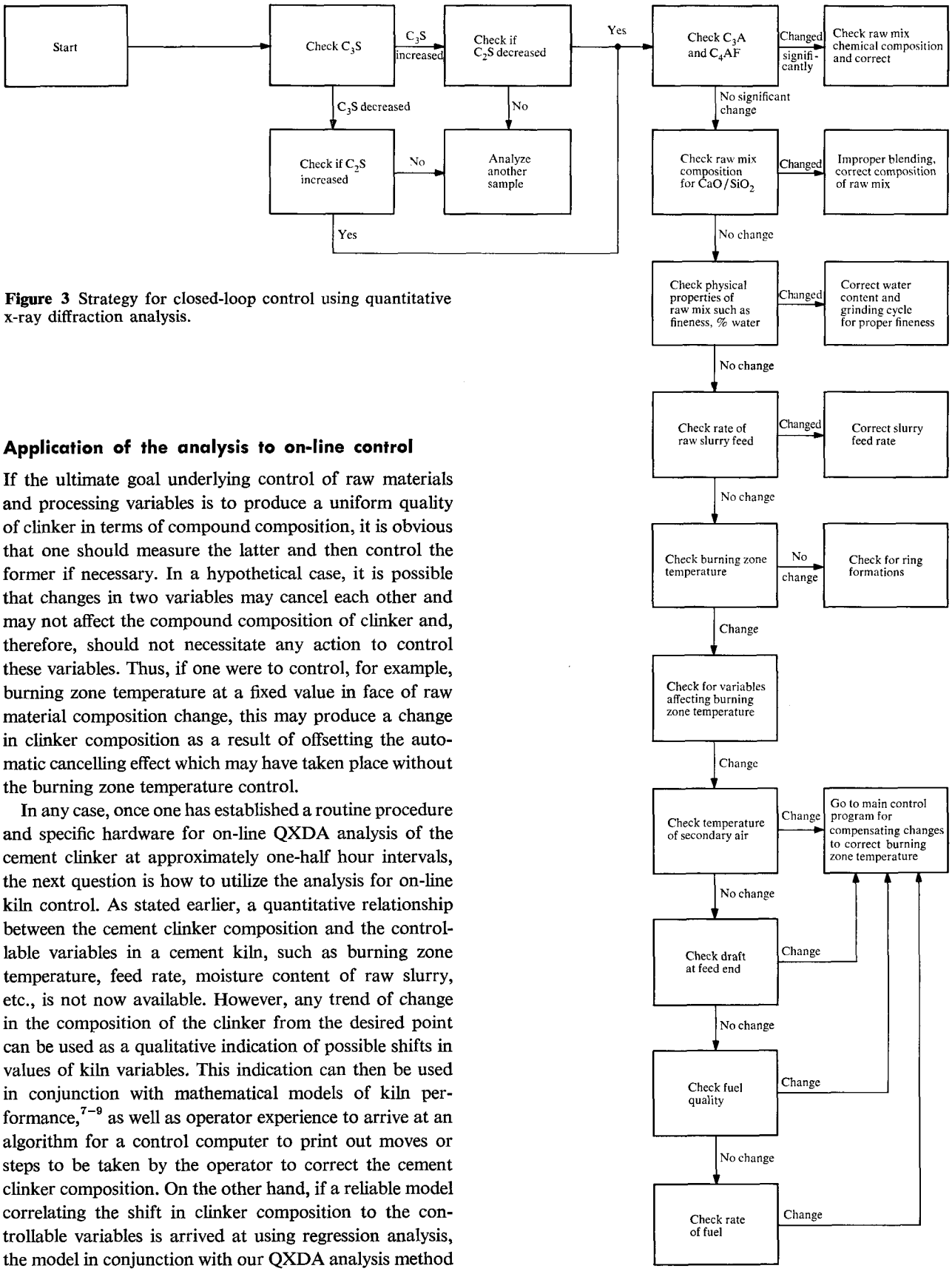


Figure 3 Strategy for closed-loop control using quantitative x-ray diffraction analysis.

Application of the analysis to on-line control

If the ultimate goal underlying control of raw materials and processing variables is to produce a uniform quality of clinker in terms of compound composition, it is obvious that one should measure the latter and then control the former if necessary. In a hypothetical case, it is possible that changes in two variables may cancel each other and may not affect the compound composition of clinker and, therefore, should not necessitate any action to control these variables. Thus, if one were to control, for example, burning zone temperature at a fixed value in face of raw material composition change, this may produce a change in clinker composition as a result of offsetting the automatic cancelling effect which may have taken place without the burning zone temperature control.

In any case, once one has established a routine procedure and specific hardware for on-line QXDA analysis of the cement clinker at approximately one-half hour intervals, the next question is how to utilize the analysis for on-line kiln control. As stated earlier, a quantitative relationship between the cement clinker composition and the controllable variables in a cement kiln, such as burning zone temperature, feed rate, moisture content of raw slurry, etc., is not now available. However, any trend of change in the composition of the clinker from the desired point can be used as a qualitative indication of possible shifts in values of kiln variables. This indication can then be used in conjunction with mathematical models of kiln performance,[7–9] as well as operator experience to arrive at an algorithm for a control computer to print out moves or steps to be taken by the operator to correct the cement clinker composition. On the other hand, if a reliable model correlating the shift in clinker composition to the controllable variables is arrived at using regression analysis, the model in conjunction with our QXDA analysis method

Table 5 Effect of variation in oxide content on clinker composition

Raw Mix Oxides	*Percent of Oxide (Ignited Basis)*		
	Case I	*Case II*	*Case III*
SiO_2	22.2	23.2	22.2
Al_2O_3	5.8	5.8	6.8
Fe_2O_3	3.1	3.1	2.1
CaO	64.9	63.9	64.9
MgO	4.0	4.0	4.0
Clinker Compounds	*Percent of Compound (Potential Composition)*		
C_3S	52.0	40.5	47.0
C_2S	24.5	36.0	28.0
C_3A	10.0	10.0	14.5
C_4AF	9.5	9.5	6.5

Case I: Normal raw mix for Type I cement.
Case II: Deviation in normal raw mix composition in terms of increase in SiO_2 content by one percent and decrease in CaO content by one percent (note 11.5% difference in C_3S and C_2S quantities).
Case III: Deviation in normal raw mix composition in terms of increase in Al_2O_3 content by one percent and decrease in Fe_2O_3 content by one percent (note that all the four phases are affected).

can be used for closed-loop control of a cement kiln. The QXDA method, by itself, provides a tool to obtain such a regression model.

Without going into any elaborate detail, the illustration in Fig. 3 gives a strategy for detecting the cause of shift in clinker composition which can be used for kiln control. A case study in Table 5 shows how slight variations in oxide content of raw mix can significantly affect the composition of clinker.

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