**A. P. Iribarne**
Department of Chemical Engineering.

**J. V. Iribarne**
Department of Physics,
60 Saint George Street.

University of Toronto,
Toronto, Ontario, Canada M5S 1A7

**E. J. Anthony**
CANMET,
Energy, Mines and Resources Canada,
Ottawa, Ontario, Canada

**J. Blondin**
CERCHAR,
Charbonnages de France,
Mazingarbe, France

# The Phase Analysis of Coal Combustion Ashes

*The phase composition of coal combustion ashes is important in regard to their potential uses. Here it is shown that a combination of phase separation techniques with X-ray diffraction, thermogravimetric analysis, and conventional chemical analysis, including elemental analysis and wet chemistry, can be used to obtain a fairly complete phase composition. The application of these techniques is illustrated with an FBC ash sample, indicating the procedures used to achieve the identification of calcium silicates, aluminates and ferrites, and their quantitative estimates. A new method for the quantitative determination of CaO in presence of large amounts of $Ca(OH)_2$ has been developed which uses phase separation as a previous step to chemical titration.*

## I Introduction

Ash handling and disposal is a basic problem in a coal combustion power plant. In particular, large volumes of ash are generated by advanced combustion technologies, such as fluidized bed combustors which use limestone as a $SO_2$ sorbent. Various possibilities have been investigated on the utilization of these residues: use in building and structural materials (cements and mortars, concretes, etc.), use in agriculture as liming agent or soil nutrient, use in neutralization of acidic wastes, etc. Concern for this problem has motivated numerous publications; among others: EPRI (1991), Berry et al., (1987), Lotze and Wargalla (1985), Jahn and Weis (1989), Merriam and Cousens (1993). A summary can be found in Smith (1990).

Utilization of fluidized bed combustion residues must take into account a variety of physical and chemical properties. Thus, the study of these properties constitute an essential field of research. The cementitious properties of coal combustion ashes are particularly important for their potential utilization. These properties depend on their phase composition; however, while the elementary chemical composition is readily obtained, the phase analysis presents some difficulties. In particular, certain calcium compounds (silicates, aluminates, ferrites) are hardly observable by direct X-ray diffraction scanning, even though these compounds may represent an important fraction of the material. In the case of residues from fluidized bed combustion (FBC) where limestone is used for retention of the sulfur from coal, after determining the contents in CaO, $Ca(OH)_2$, $CaSO_4$, and $CaCO_3$, as much as 30 or 40 percent of the total calcium may remain unaccounted for. The direct scanning diffractogram appears dominated by other compounds (e.g., silica, lime, anhydrite) and any calcium silicates, aluminates, or ferrites are not detectable or only suggested by small peaks mostly interfered with or covered by the patterns of the main phases.

The purpose of this work is to show that a judicious combination of grinding preparation, physical separation of phases, and wet chemistry methods with instrumental analysis can succeed in providing much more complete information, both qualitative and quantitative, about the phase composition (see also Iribarne et al., 1993).

The method used to obtain maximum information must be adapted to the characteristics of the material studied. As an example, these methods have been applied to the study of samples from the pilot-scale circulating fluidized bed combustion (CFBC) plant operated by the Canada Centre for Mineral and Energy Technology (CANMET). The ashes obtained from this pilot plant were produced to simulate those that might be generated by Nova Scotia Power's 165 MWe Point Aconi generating station in Nova Scotia.

First the methods of phase separation available will be described (Section II) and their efficiency in permitting X-ray diffraction to reveal various phases not detectable by direct scanning will be illustrated by work done on the aforementioned sample (Section III). Then the integration of the information obtained with the results of more conventional methods of analysis will be considered (Section IV). Section V will deal with the quantitative estimate of calcium silicates, aluminates, or ferrites. Finally, a new method for determination of CaO in presence of large amounts of $Ca(OH)_2$ is described in Section VI.

## II Methods of Phase Separation

The methods to be described assume a previous preparation of the sample by adequate grinding. Usually it is sufficient to grind to mesh 200 (particle size < 75 μm); in certain cases, grinding to mesh 400 (< 45 μm) may be preferable.

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Table 1 Densities (g/cm$^3$)

| | |
|---|---|
| CH | 2.24 |
| Feldspars, quartz, anhydrite, mica | 2.54–2.80 |
| Various calcium compounds: CS, $C_3A_5$, $C_2A$, CA, $C_3S_2$, $C_2SA$ (gehlenite), $C_3A$, $C_5A_3$, $C_3S$, $C_2S$ (larnite) | 2.88–3.28 |
| C (free CaO) | 3.34 |
| Ferrites and aluminoferrites: $C_2F$, CF, $C_2(F,A)$ | 3.98–5.08 |
| Iron oxides | 5.18–5.24 |
| (where C = CaO, A = $Al_2O_3$, S = $SiO_2$, F = $Fe_2O_3$, H = $H_2O$, as used in cement notation) | |

(*a*) The difference in solubilities of the material components can help in the phase separation. Water extraction at properly chosen conditions (room temperature, one to several hours with continuous stirring) can remove soluble or slightly soluble phases without appreciably affecting other phases, such as calcium silicates, aluminates, or ferrites.

When applying water extraction, judgment should be exerted as to the duration of the treatment. For compounds of the group of calcium silicates, aluminates, or ferrites, hydration of the order of 10 percent of certain compounds may be expected in a period of a few hours. Work done by Lerch and Bogue (1927) showed that, for most of these compounds, an appreciable water attack requires times of the order of days or weeks. This is dependent on the compound (for instance, tricalcium silicate, $C_3S$ in cement notation, is easily attacked, while gehlenite $C_2AS$ is stable) and on the presence of other compounds in the mixture (see Odler and Abdul-Maula, 1987; also, Taylor, 1990, Section 5.6). Only some compounds, such as $C_{12}A_7$ may be destroyed. Moore (1976) applied this technique to cement, with an extraction time of 40 min.

A limited attack is not objectionable for qualitative identification. Water extraction allows the elimination of CaO, $Ca(OH)_2$, and most of the $CaSO_4$ in order to facilitate the study of the residual phases. For quantitative purposes, an adequate time limitation should be chosen for the water treatment.

(*b*) Density separation is also a powerful tool. Quartz, calcium hydroxide, light silicates such as kaolinite, mica, and various feldspars, anhydrite, and calcite can be separated from most calcium silicates, aluminates, and ferrites from a suspension of the sample in a liquid of an appropriate intermediate density (e.g., 2.85 g/cm$^3$). The former compounds will then have smaller densities than the liquid, while the latter, as well as quicklime, corundum, and iron oxides, are heavier. Table 1 gives an indication of some relevant density values. The separation is accelerated by centrifugation. The lime may have been previously eliminated by water extraction, as already mentioned.

(*c*) Use of magnetic techniques can separate the ferrites and iron oxides from either the original sample or from the samples previously treated by other techniques.

(*d*) Sieving separates fractions of different composition, according to the hardness of the components. For instance, sieving is commonly used by X-ray diffraction operators to decrease the proportion of quartz, which is harder to grind to fine sizes than the other components.

(*e*) Use of selective solvents eliminate certain compounds; for instance, maleic acid or salicylic acid are used to eliminate soluble silicates. See, e.g., the summary on selective dissolution by Klemm and Skalny (1977).

The exact application of these techniques must depend on the case in study. In the example of treatment of a sample of FBC ashes described in the following sections, the exact technique used will be described in each step.

## III X-Ray Diffraction Studies

A series of XRD tests combined with phase separations were made in order to obtain a qualitative identification of all the significant phases present.

The sample chosen to illustrate the possibilities of these techniques consists of bed ashes from FBC, hydrated by the CERCHAR procedure (Blondin, 1991; and Blondin et al., 1993) and previously studied and discussed by Iribarne (1991). The combustion temperatures in the fluidized bed were about 850°C. Table 5 gives the elemental composition of the sample.

X-ray powder diffraction was performed with a Philips Model 1820 fully automated diffraction system with EDS monochromatized Cu Kα radiation, and also with a Siemens D 500 with Cu filtered radiation and Kevex detector. The sample was previously ground to 200 mesh.

The direct observation gave diffractogram of Fig. 1, dominated by the peaks of quartz ($SiO_2$ or S in cement notation), anhydrite ($CaSO_4$ or $C\bar{S}$ in cement notation), and portlandite ($Ca(OH)_2$ or CH in cement notation). A system of small peaks (at 2θ angles between 31 and 34 deg) only suggests the presence of other compounds. The sample was then extracted with $CO_2$-free water at room temperature with continuous stirring and under $N_2$ atmosphere, for 6 h, renewing the water by decantation and filtration every 1 to 2 h; the volume of the water should be large enough, considering the low solubilities of $Ca(OH)_2$ and $CaSO_4$: between 500 and 800 mL in each extraction, for about 5 g of sample were used. The insoluble material was then filtered and dried. The amount of residual $Ca(OH)_2$ in the filtrate can be checked by acidimetry. After this treatment, the diffractogram of Fig. 2 was obtained from the residual sample; now portlandite and anhydrite have disappeared, and the system at angles 31 to 34 deg appears better defined, but quartz is still the dominating phase, and consequently the other peaks still appear depressed.

Density separation was then performed using a liquid of density 2.86 g/cm$^3$. The sample is introduced into the centrifuge tube, the tube is stoppered and shaken vigorously to disperse the sample, and centrifugation is performed; when the powder is ground to very fine particles, agglomerates tend to form and must be dispersed with ultrasound (needle dismembrator) prior to centrifugation. The liquid was prepared by mixing small amounts of acetone with s-tetrabromoethane (TBE) (of density 2.97 g/cm$^3$). Either the lighter or the heavier fraction can then be separated for analysis. In the present case, the lighter fraction was discarded and, after decantation of the liquid, the heavy residue was washed twice with acetone. For this purpose, the residue was dispersed each time in acetone in the same tube, centrifuged and the acetone decanted. The TBE was thus eliminated. The washed residue was then dried and analyzed. TBE does not react with the components of the sample under the conditions of the operation.

Most of the quartz was now eliminated and the diffractogram of Fig. 3 was obtained, showing clearly three phases (apart from some residual quartz) which, according to the following discussion, appear to be: ferrite ($2CaO \cdot (Fe, Al)_2O_3$ or $C_2(F, A)$ in cement notation), larnite ($\beta$-$2CaO \cdot SiO_2$ or $C_2S$), and gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$ or $C_2AS$). Figure 4 shows the same diffractogram on an extended scale, where the group of peaks for 2θ between 31 and 34 deg can be better observed.

The sample was then extracted with a solution of 20 percent of maleic acid in methanol (Tabikh and Weht, 1971), filtered, and dried. The residue was again analyzed. Use of maleic acid has the effect of eliminating the larnite, leaving gehlenite and ferrite; this is shown in Fig. 5. It will be noticed that the peak pattern of the ferrite is now clearly seen.

In summary, critical consideration of the patterns observed in these diffractograms indicate the following:

1 The characteristic diffraction pattern of ferrite shows that it is present, possibly with some substitution of Fe by Al.

2 Larnite is confirmed to be present in some crystalline form not precisely identified. It may be mentioned that the presence of larnite in a similar material was first detected by infrared absorption (Blondin, 1992).

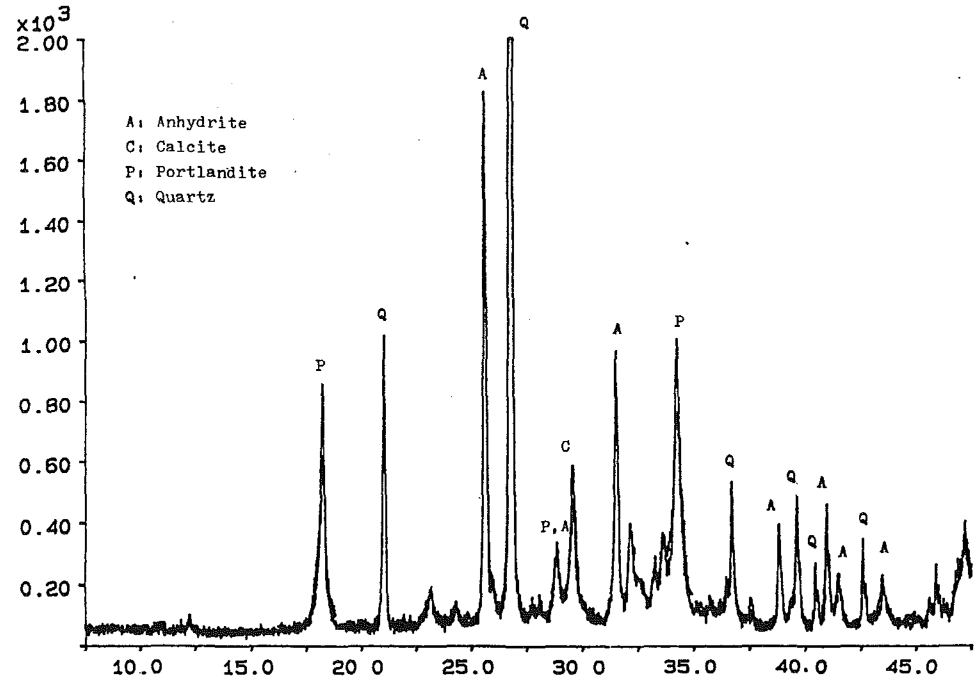

Fig. 1 X-ray diffraction—direct scanning of sample

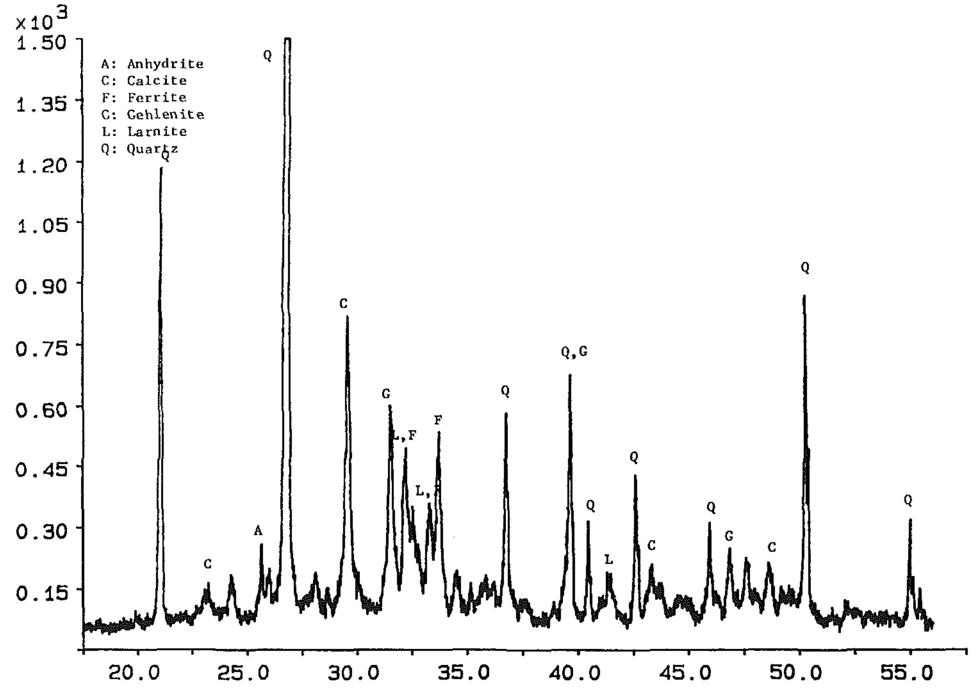

Fig. 2 X-ray diffraction—after water extraction

3 A compound, clearly different from ferrite and larnite, is characterized by one of the strongest peaks in the pattern, at 0.2857 nm. Gehlenite has been reported to have a strongly predominant peak situated, according to different authors, between 0.2845 and 0.2857 (see, e.g., Louisnathan, 1971). No association of this peak could be found to any other significant peaks that could relate it to compounds other than gehlenite. On the other hand, this is the only gehlenite peak which is not overlapped by others along the pattern trace. Thus, although the presence of gehlenite cannot be demonstrated with absolute certainty, it appears as the only interpretation consistent with the XRD patterns obtained. It is interesting to note that gehlenite is a high-temperature compound, and must form in the hotter regions existing within the fluidized bed, i.e., in hot spots or on coal particle surfaces (see, e.g., Davidson et al., 1985; Hamer, 1986; Hansen, 1991; Yates, 1983, Couturier et al., 1991).

For confirmation purposes, these patterns were also compared with those obtained from standards of gehlenite, larnite, and aluminoferrite ($C_4FA$) provided by Construction Technology Laboratories, Inc., Skokie, IL, U.S.A.

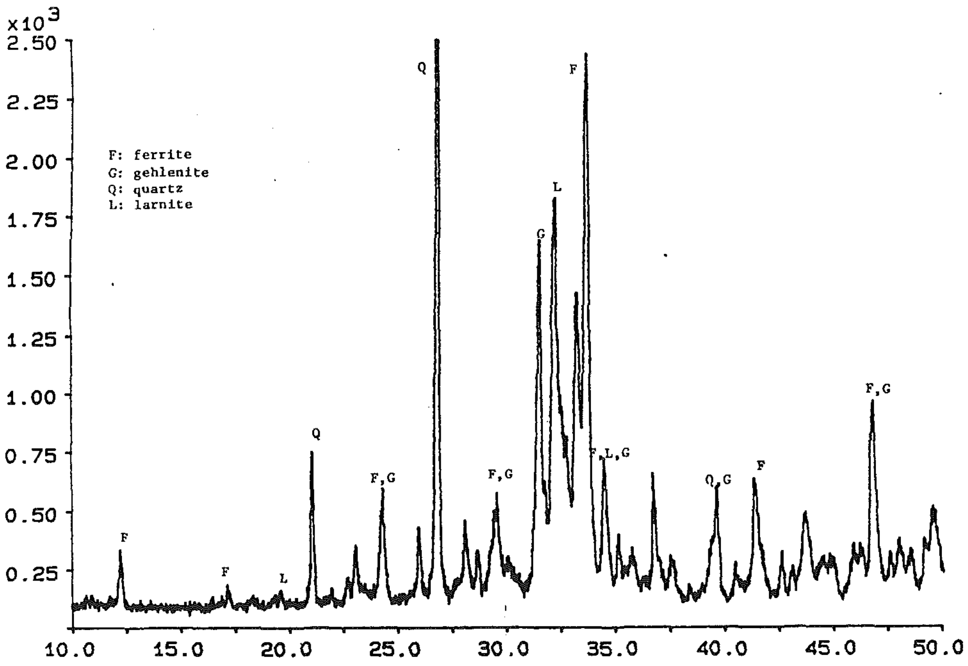

Fig. 3 X-ray diffraction—after water extraction and density separation

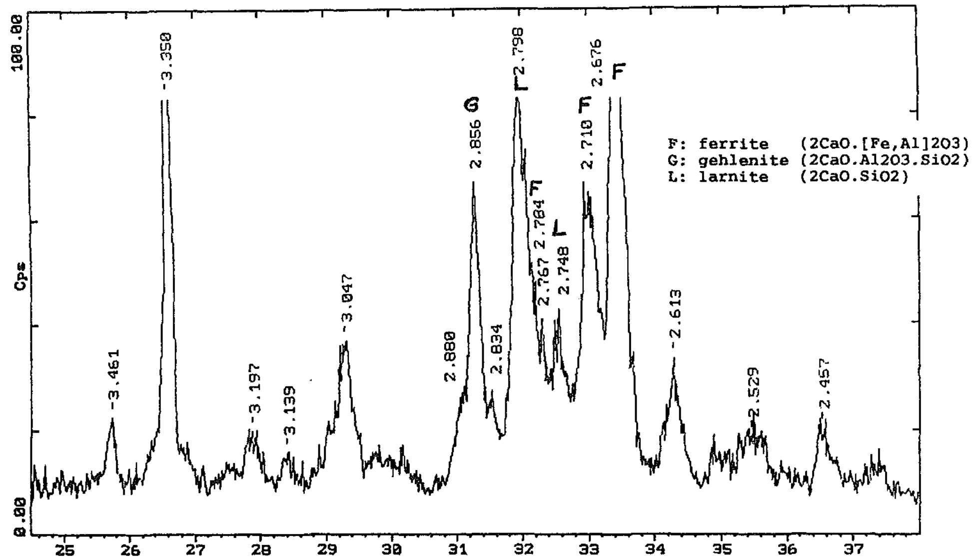

Fig. 4 As Fig. 3, in extended scale. Figures on peaks indicate parameter *d* in Angströms.

## IV Integration With Instrumental and Wet Methods of Chemical Analysis

In order to obtain as much knowledge as possible about the phase composition of the samples, the information obtained by the methods just discussed must be integrated with the chemical information from both instrumental and wet chemistry. A brief summary of the successive steps taken to obtain information about the phase composition will now be given.

**1 Elemental Analysis.** It is normal to obtain the elemental analysis (with the elements usually expressed as oxides) from either X-ray fluorescence, induced plasma, or neutron activation, to which determinations of total S and total C can also be added (e.g., using LECO furnace and infrared detection).

**2 Wet Chemistry and Determination of Anions.** Sulfate ($SO_4^{2-}$), sulfide ($S^{2-}$), and carbonate ($CO_3^{2-}$) can be determined by various methods. It is usually assumed that these anions are associated mainly with $Ca^{2+}$ and that the analysis can be taken as indicating the content of the phases $CaSO_4$, $CaCO_3$, and CaS. If the abundance of Mg is appreciable, the corresponding compounds must also be taken into account. Other compounds, such as $Na_2SO_4$, etc., are usually minor contributions and can be neglected.

**3 Free Lime (F.L.)** By free lime is understood the sum [$CaO + Ca(OH)_2$], both compounds expressed as CaO percent. There are methods to determine this parameter; see, for instance, Franke (1941); method of sucrose, as in ASTM C-25, lime index; etc. In order to differentiate the two components, it is customary to derive $Ca(OH)_2$ from thermogravimetric analysis. However, CaO must then be obtained by difference, and when its amount is much less than that of $Ca(OH)_2$, as in the case of hydrated ashes, say, by the aforementioned CERCHAR method, the value is a small difference between two larger numbers; as the errors of F.L. and of $Ca(OH)_2$ are of the order of units percent, the error for CaO turns out to be of the same order of magnitude as its value.

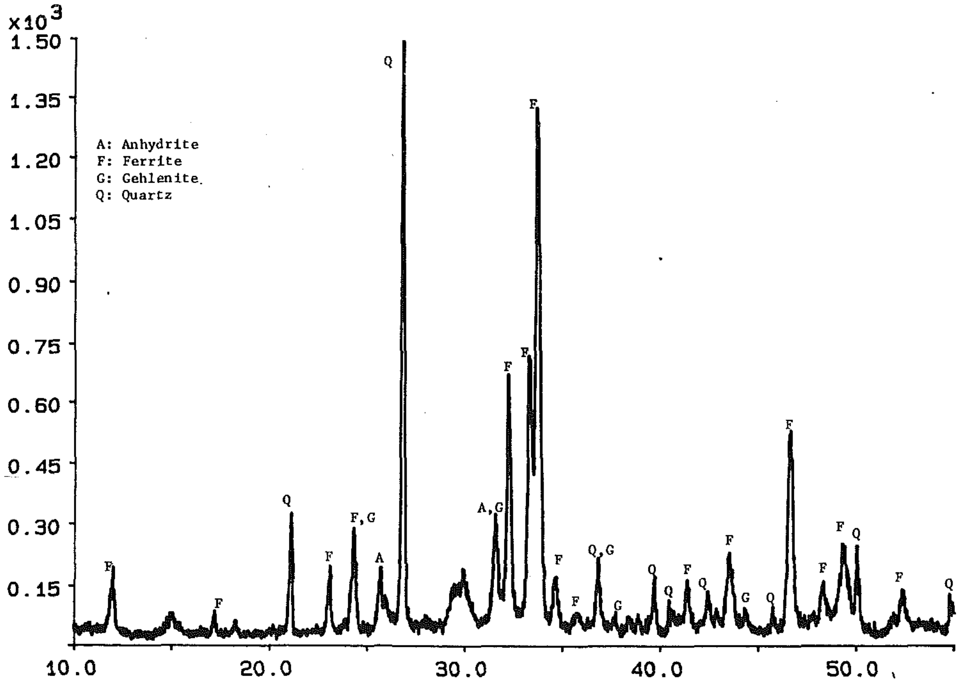

Fig. 5 X-ray diffraction—after water extraction, density separation, and maleic acid extraction

This unsatisfactory situation is resolved by the use of the new method for CaO determination described in Section V.

Thus, the procedure to differentiate the two components of F.L. varies according to their relative amounts. If $Ca(OH)_2$ is of the same order as CaO or smaller, it is derived from TGA and CaO is obtained by difference ($CaO = F.L. - Ca(OH)_2$). If CaO is much less abundant than $Ca(OH)_2$, it should be determined by the separation method described in Section V, and $Ca(OH)_2$ derived by difference ($Ca(OH)_2 = F.L. - CaO$).

**4 Total Alkalinity (T.A).** Total alkalinity is defined as the alkalinity found by digesting the sample with 1 N HCl and back titrating with 1 N NaOH with phenolphthalein as indicator. This titration includes CaO, $CaCO_3$, and all other phases soluble in the digestion conditions, which includes most calcium silicates, aluminates, and ferrites, even water-resistant compounds like gehlenite; for instance, if the ferrite, larnite, and gehlenite are considered (as in the aforementioned sample; see Section V)

$$2CaO \cdot (Fe, Al)_2O_3 + 10\,H^+ = 2\,Ca^{2+} + 2\,(Fe, Al)^{3+} + 5\,H_2O$$

followed in the back titration by

$$2\,(Fe, Al)^{3+} + 6\,OH^- = 2\,(Fe, Al)\,(OH)_3,$$

$$2CaO \cdot SiO_2 + 4\,H^+ = 2\,Ca^{2+} + 2\,H_2O + SiO_2,$$

$$2CaO \cdot Al_2\,O_3 \cdot SiO_2 + 10\,H^+ = 2\,Ca^{2+} + 2\,Al^{3+} + 5\,H_2O + SiO_2$$

followed in the back titration by

$$2\,Al^{3+} + 6\,OH^- = 2\,Al(OH)_3$$

$Fe_2O_3$ and $Al_2O_3$ are not included in the final result, since $Fe^{3+}$ and $Al^{3+}$ reprecipitate before the end point of the return titration.

T.A. can be expressed as the sum

$$T.A. = CaO + Ca(OH)_2 + CaCO_3 + OCC$$

(terms for MgO and $MgCO_3$ should be added if present in appreciable concentrations) where all terms are expressed as CaO, and OCC stands for other calcium compounds. OCC is then obtained, expressed in terms of CaO, by subtracting F.L. and $CaCO_3$ from T.A.

**5 Calcium Balance.** With the collected information discussed in the foregoing, the sum of $CaSO_4$ (expressed as CaO) and T.A. can be compared with the total CaO from the elemental analysis. They should be equal, thus providing a quantitative check of the phase determinations. However, some calcium compounds insoluble in 1 N HCl may also be present, in which case a more general equation should be written

$$\text{Total CaO} = CaSO_4 + T.A. + AICC$$

where AICC stands for any "acid insoluble calcium compounds." These compounds are not common, but some example, like diopside ($CaO \cdot MgO \cdot 2SiO_2$), may be present.

Table 2 indicates schematically the various phases or groups of phases, and the analytical determinations from which they are derived.

In summary, the route followed to this point allows quantitative determination of the phases $CaSO_4$, CaS, $CaCO_3$, CaO, and $Ca(OH)_2$. The "other calcium compounds" OCC (gehlenite, larnite, and ferrite in the sample chosen as illustration) have been identified. However, they have only been determined quantitatively as a group, in terms of CaO. The problem remains in obtaining at least an approximate quantitative estimate of each of these compounds. We will not consider here the less likely case of acid insoluble calcium compounds (AICC).

## V Quantitative Estimate of the "Other Calcium Compounds"

In the previous calculations, this group (OCC) is determined only collectively, expressed as CaO. Once the components have been properly identified by XRD coupled with the phase separation techniques, a quantitative estimate of the various components can be attempted. This may not always be possible, and when possible, it requires a rather elaborate procedure, which must be adjusted in each case to the particular compounds present in the sample; therefore, rather than attempting to establish a procedure of general validity, work done on the selected chosen sample will be described as an illustration. Appropriate variations should be introduced in other cases.

**1 The Ferrite Composition.** The exact stoichiometry of some of the calcium silicates, aluminates, and ferrites is not always

**Table 2 Phases included in each of the chemical determinations**

| Phases: Analysis | $CaSO_4$ | Ca | CaO | $Ca(OH)_2$ | $CaCO_3$ | OCC | AlCC |
|---|---|---|---|---|---|---|---|
| Total CaO | X | X | X | X | X | X | X |
| T.A. | | X | X | X | X | X | |
| F.L. | | | X | X | | | |
| $SO4^{2-}$ | X | | | | | | |
| $S^{2-}$ | | X | | | | | |
| $CO3^{2-}$ | | | | | X | | |
| TGA | | | | X | | | |
| CaO (direct method) | | | X | | | | |

known. In particular, substitution of Fe by Al in the dicalcium ferrite leads to a series of solid solutions that can be expressed as $2CaO \cdot [Fe_{(1-x)}Al_x]_2O_3$, where $x$ is the fraction of Fe atoms that have been replaced by Al atoms.

In clinker ferrite, $x$ may be of the order of 0.5 or greater (Taylor, 1990), while the alumina ratio $Al_2O_3/Fe_2O_3$ is in the range of 1 to 4 in normal Portland cement clinkers. However, in our chosen sample, this ratio is 0.95. This suggests that low values of $x$ are therefore to be expected.

The change in composition of the ferrite causes a shifting of the diffraction peaks. In order to obtain a rough estimate of $x$, an exact measurement of the $d$ values of significant peaks in the XRD spectrum can be compared with those of known standards. The shifting of these peaks with $x$ can then be used for interpolation or extrapolation. Considering the patterns of standards of composition $C_6AF_2$ and $C_4AF$ (cement notation) and comparing with that of the sample studied for the peaks of crystallographic indices ($h$, $k$, $l$): (2, 0, 0), (0, 0, 2), (1, 4, 1), and (0, 8, 0), it was possible to conclude, as a rough estimate, that $x$ should have a very low value, probably around 0.1 (and in any case, between 0 and 0.3).

**2 Method of Stoichiometric Equations.** In order to apply the method of stoichiometric equations—similar to Bogue's calculations for cement (see Taylor, 1990)—it is necessary to separate as well as possible the set of compounds (OCC) from the rest of the phases. This is done by the methods of water extraction and density separation described in Section III of this paper. The residue obtained must be scanned by XRD (cf. Fig. 3) and subjected to an elemental analysis indicating the values of CaO, $SiO_2$, $Al_2O_3$, and $Fe_2O_3$ percent.

In the separated residue obtained from the sample used for illustration, XRD revealed the presence of gehlenite, larnite, ferrite, magnetite, and some residual quartz. The following set of equations can therefore be written:

$$
\begin{aligned}
\text{CaO percent} &= (2CaO/2CaO\cdot Al_2O_3 \cdot SiO_2)\,G \\
&\quad + (2CaO/2CaO\cdot SiO_2)\,L \\
&\quad + \{2CaO/[(1\text{-}x)\,2CaO\cdot Fe_2O_3 \\
&\quad + x\,2CaO\cdot Al_2O_3]\}\,F \\
SiO_2\text{ percent} &= (SiO_2/2CaO\cdot Al_2O_3 \cdot SiO_2)\,G \\
&\quad + (SiO_2/2CaO\cdot SiO_2)\,L + Q \\
Al_2O_3\text{ percent} &= (Al_2O_3/2CaO\cdot Al_2O_3\cdot SiO_2)\,G \\
&\quad + \{x\,Al_2O_3/[(1\text{-}x)\,2CaO\cdot Fe_2O_3) \\
&\quad + x\,2CaO\cdot Al_2O_3]\}\,F \\
Fe_2O_3\text{ percent} &= \{(1\text{-}x)\,Fe_2O_3/[(1\text{-}x)\,2CaO\cdot Fe_2O_3 \\
&\quad + x\,2CaO\cdot Al_2O_3]\}\,F \\
&\quad + ((3/2)Fe_2O_3/Fe_3O_4)\,M
\end{aligned}
$$

In this system of equations, the left sides are the data from analysis, the chemical formulas stand for their molecular weights, and G, L, F, M, and Q are the percent weights of gehlenite, larnite, ferrite, magnetite, and quartz in the separated residue, respectively. There are six unknowns: G, L, F, M, Q, and $x$. Since there are only 4 equations, two unknowns must be separately determined. It is assumed that $x = 0.1$, following the previous discussion. Regarding Q, it has been estimated as between 5 and 8 percent by QXRD, and consequently is ascribed a value of Q = 6.5 percent. Using these values for $x$ and Q, computing the stoichiometric ratios, and writing the reduced system in matrix form:

$$
\begin{pmatrix} 0.4090 & 0.6512 & 0.4215 & 0 \\ 0.2191 & 0.3488 & 0 & 0 \\ 0.3718 & 0 & 0.0383 & 0 \\ 0 & 0 & 0.5401 & 1.0345 \end{pmatrix}
\begin{pmatrix} G \\ L \\ F \\ M \end{pmatrix}
=
\begin{pmatrix} \text{CaO percent} \\ SiO_2\text{-6.5 percent} \\ Al_2O_3\text{ percent} \\ Fe_2O_3\text{ percent} \end{pmatrix}
$$

This system can be solved by a number of known methods; e.g., by finding the inverse matrix (Pipes, 1958). The result is:

G = 9.2 percent
L = 30.1 percent
F = 25.2 percent
M = 9.2 percent

Or, since only the relative abundances of the first three compounds is of interest, the percentages can be referred to their sum, to indicate their relative abundance (obviously valid for the original sample, as well as for the separated residue containing the OCC):

G = 15 percent
L = 46 percent
F = 39 percent

totaling 100 percent. The sum OCC = G + L + F is known (Section IV); therefore, the individual contents of gehlenite, larnite, and ferrite in the original sample are now easily estimated.

Obviously, the approximations or assumptions adopted influence the result. G is particularly sensitive to changes; for instance, it becomes 19 percent if $x = 0.25$, while L becomes 42 percent and F remains unchanged. However, as a first step, this method gives estimates of these components, which would otherwise be unobtainable.

In order to incorporate this result into the phase composition of the original sample, it should be recalled that the total of OCC (in this case, the sum of G, L, and F) is derived from chemical analyses in terms of CaO. For the illustration sample, this amounted to 10.5 percent of the sample. The previous result for relative abundances of the three compounds can also be expressed in terms of CaO, so that the distribution of this 10.5 percent can be calculated, and from it, the percentages of the three compounds (expressed as such) in the original sample can be derived. In the chosen example, the result is:

G = 3 percent of the sample
L = 9 percent of the sample
F = 8 percent of the sample

where the values have been rounded to unit values, since the approximation of the method does not allow better precision.

This completes the phase composition as shown in Table 6.

**3 Method of Extractions.** The method of equations, as described, is laborious and only limited accuracy can be expected. A simpler procedure, not requiring XRD and of comparable accuracy, can also be followed.

As an initial step, a water extraction of the sample is performed, as indicated in Section II. Most of the lime and the $CaSO_4$ is eliminated in this way, while the attack on silicates or ferrites is very limited and can be ignored in this approximation (notice that tricalcium silicate, which is less resistant, is not present in FBC ashes). The residue is then subject to the following analyses:

(*a*) T.A.
(*b*) F.L.

(*c*) Determination of sulfate in the residue.

(*d*) Treatment with 5 percent $H_3BO_3$ solution (cf. Moore, 1976). A known amount of about 0.2 g is stirred in 80 mL of boric acid solution at room temperature for 2 h, filtered, washed, and the liquid brought to volume (say, 100 mL). $Ca^{2+}$ is determined in the liquid (in this study, this was done both by neutron activation and by induced coupled plasma).

(*e*) Treatment with KOSH solution (10 percent KOH + 10 percent sucrose (cf. Gutteridge, 1979). A known amount of 0.2 g is treated with 50 mL of KOSH boiling solution for 2 min, filtered with vacuum, washed, and the liquid brought to volume. $Ca^{2+}$ is determined in the liquid.

The calcium extracted with boric acid is corrected from the lime (F.L.) (analysis *b*) and from the $CaSO_4$ (analysis *c*), which dissolve in the boric solution. The difference corresponds to larnite, which also dissolves (while gehlenite and ferrite remain unattacked).

The calcium extracted with KOSH is corrected from the $CaSO_4$ (analysis *c*), which dissolves in the reagent. The difference corresponds to ferrite, which also dissolves (while gehlenite and larnite remain unattacked).

Thus, analyses *d* (corrected from *b* and *c*) and *e* (corrected from *c*) give the content of larnite and of ferrite in the residue from water extraction. The difference (T.A. − F.L.) indicates the sum of (G + L + F), expressed in terms of CaO. Since L and F are known, G may be derived. Obviously, appropriate stoichiometric ratios are used to relate percentages expressed as CaO and percentages expressed in terms of the corresponding compounds.

Table 3 may help to clarify the calculations done with the results of the analyses performed on the water-extracted sample. The crosses indicate the compounds determined in each analysis.

These methods were first checked with standards for gehlenite, larnite, and ferrite (from Construction Technology Laboratories) with satisfactory results, and then applied to the sample selected for illustration.

For the chosen sample, the following results were obtained with these techniques:

G = 20 percent
L = 48 percent
F = 33 percent

with the figures referred to the sum of the three compounds taken as 100 percent, i.e., indicating their relatives abundances.

By comparing with OCC and doing the same calculations indicated in Section 2, the percentages of the three compounds in the sample, expressed as such, can be obtained:

G = 4 percent of the sample
L = 8 percent of the sample
F = 9 percent of the sample

It can be seen that, within the limited accuracy of these estimates, this result gives a very satisfactory agreement with that obtained by the method employing the stoichiometric equations.

## VI Determination of Free Calcium Oxide

The technique of separation by density has another important possible application. No method exists to determine CaO in the presence of $Ca(OH)_2$. However, the problem is important in the analysis of FBC residues, particularly after a hydration process has been applied to the material. The difference of densities between the two compounds (see Table 1) provides the base for a new quantitative method.

The density of CaO is 3.34 g/cm$^3$; that of $Ca(OH)_2$, 2.24 g/cm$^3$. Density separation therefore provides an appropriate method to eliminate $Ca(OH)_2$ before analyzing CaO. The liquid to be used must be of some intermediate density. During centrifugation, $Ca(OH)_2$ goes to the top with other light compounds, while CaO is accumulated at the bottom, with the heavy fraction.

Table 3 Analyses used for the determination of OCC

| Analysis | Residual lime | Residual anhydrite | Larnite | Gehlenite | Ferrite |
|---|---|---|---|---|---|
| (*a*) T.A. | X | | X | X | X |
| (*b*) F.L. | X | | | | |
| (*c*) $SO_4^{2-}$ | | X | | | |
| (*d*) $H_3BO_3$ | X | X | X | | |
| (*e*) KOSH | | X | | | X |

The procedure is as follows. A sample is weighed, not exceeding 0.15 g for each 10 mL of the liquid to be used, and introduced into a centrifuge tube. The liquid is added, the tube is stoppered and strongly shaken in order to disperse the powder in the liquid. After centrifuging to separate the fractions lighter and heavier than the liquid, the upper, lighter fraction is removed, the liquid is decanted, and the residue is washed with acetone, by centrifugation and decantation, in order to eliminate the TBE. The washed residue is collected in water and its lime content is measured. In the present experiments, this measurement was done by sugar extraction, following the indications of the norm ASTM C-25 for the determination of the "lime index," but filtrating the liquid before acidimetric titration.

In order to prepare known samples to test the method, two reference materials were used, prepared with FBC ashes, so as to have an appropriate matrix. One of them was a fly ash from FBC with high content of CaO (35.5 percent); this was heated in a furnace to 600°C before use, to eliminate any $Ca(OH)_2$ and $CaCO_3$. The other was a hydrated FBC ash (by the aforementioned CERCHAR process), further treated in boiling $CO_2$-free water for 2 min, filtered and dried, so that free CaO was reduced to about 0.02 percent. Three series of measurements were done on samples obtained by taking in the centrifuge tube variable amounts of each of the two reference materials. Two other series were done by repeating measurement on a reference sample produced by thoroughly mixing the two materials in known proportions.

Table 4 collects the results of all the series of experiments, with indication of the conditions.

From the experience accumulated during all these tests, the following remarks can be made and the following conclusions drawn with respect to the experimental procedure:

- Grinding must be fine enough to decrease errors due to mixed particles; but it should not be finer than necessary. At an average particle size of about 5 μm, the tendency of the particles to stick to the walls of the centrifuge tubing and to agglomerate may become troublesome; in that case, ultrasound must be used to help the dispersion. Grinding to 200 mesh (particle size < 75 μm) or preferably 400 mesh (< 45 μm) should be sufficient for most materials.
- It is essential to insure a good, neat separation between the material lighter than the liquid and that denser than the liquid (containing the CaO). In order to improve the separation, times of centrifugation may be made longer (generally about 30 min should be enough), and recourse to repeated centrifugation may be appropriate. In the latter case, after the first centrifugation, the lighter material accumulated at the top is removed, more liquid is added to bring it to the same level in the centrifuge tube, the tube is again stoppered and strongly shaken to disperse the sample, and a new period of centrifugation follows. If necessary, the whole procedure may be repeated for a third time.
- It is also essential to choose an appropriate density for the liquid employed. The density of $Ca(OH)_2$ is 2.24 g/cm$^3$ and that CaO is 3.34 g/cm$^3$. It would seem that a liquid of density between 2.80 and 2.88 g/cm$^3$ is appropriate. This is obtained by mixing s-tetrabromoethane (TBE; density: 2.97 g/cm$^3$) with small amounts of acetone. Choosing too dense a liquid (for instance, pure TBE) tends to result in loss of CaO from the heavy deposit

**Table 4 Results of series of experiments**

| $n$[a] | Grinding | Temperature | Liquid density | $Ca(OH)_2$ percent | CaO percent | Percent of reference value |
|---|---|---|---|---|---|---|
| 12 | 200 mesh | Room | 2.87 | 20–25 | Various values 7.7–13.7 | 99.2 ± 4.5 |
| 8 | 200 mesh | 5°C | 2.71 | 20–25 | 10.9–14.4 and 2 Tests: 35.5 | 94.7 ± 2.6 |
| 4 | 200 mesh | Room | 2.71 | 20–25 | 9.3–13.9 | 101.0 ± 4.3 |
| 8 | Fine[b] | Room | 2.87 | 13.1 | 3.20 | 97.8 ± 14.6 |
| 10 | Fine | Room | 2.87 | 19.7 | 3.58 | 102.5 ± 8.5 |

[a] $n$: number of determinations.

[b] Fine: ground to an average size of 5 to 10 μm. (Last 2 series: tests on single sample.)

in the centrifugation, and too light of liquid may facilitate the inclusion of $Ca(OH)_2$ in the heavy deposit.

- TBE reacts with CaO in the presence of water. Therefore, after the separation by centrifugation, it must be thoroughly eliminated by washing with pure acetone (shaking, centrifuging, decanting) twice. Only then is the material treated with water for lime dosage determination.
- From the results obtained in these experiments, it appears difficult to decrease the error of the forthcoming method plus or minus several tenths of a percent (say, ± 0.3 to 0.5 percent of CaO). However, within this margin of error, the results are reliable when the aforementioned precautions have been followed.
- It may be remarked that in all of these test series, the concentration of $Ca(OH)_2$ in the samples, varying from 13 to 25 percent, were much higher than those of the CaO determined.

A further check on the performances of the new method of determination of CaO was provided by the analysis of 15 samples of FBC ashes from Gardanne, France after being hydrated in various degrees of efficiency. The free lime (CaO + $Ca(OH)_2$) was about 30 percent (expressed as CaO) in all of them. The samples were: 1) analyzed by the present method (with results varying from 3.6 to 7.0 percent), and 2) their X-ray diffraction patterns were obtained and the surfaces under the characteristic CaO peak at $d = 2.405$ Angström were measured (arbitrary units). Figure 6 shows that the correlation between the two results was excellent.

## VII Conclusions

It has been shown that by use of different techniques for the separation of phases, combined with an appropriate elaboration of the data obtained by elemental analysis and several wet chemistry techniques, it is possible to obtain a fairly complete information about the phase composition of coal combustion residues. All the main phases present may be identified and quantified; this includes phases, such as calcium silicates, aluminates, or ferrites, that presumably play an important role in the hydraulic properties of the material, whether it is used alone or blended with other materials. Also, the calcium balance, not properly accounted for in routine analyses which sometimes miss up to 40 percent of the CaO, is thereby determined in a satisfactory way.

The use of separation of phases by density has also been shown to provide a reliable method to determine directly the free CaO in materials that also contain $Ca(OH)_2$, even when this is present in much larger proportion.

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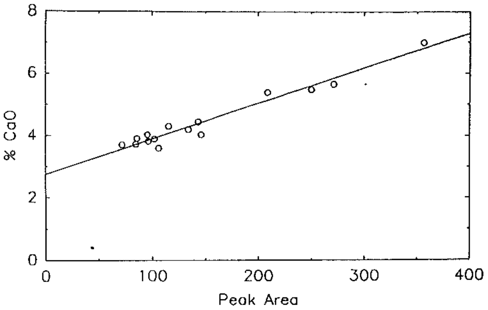

**Fig. 6 Correlation between results of CaO percent obtained by the new method and areas under CaO characteristic peak in X-ray diffraction diagrams (in arbitrary units)**

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# APPENDIX

## Composition of the FBC Sample Studied

Table 5 Elemental composition[a]

| | |
|---|---|
| $SiO_2$ | 33.8 |
| CaO | 37.0 |
| $Al_2O_3$ | 5.12 |
| MgO | 0.70 |
| $Na_2O$ | 0.09 |
| $K_2O$ | 0.62 |
| $Fe_2O_3$ | 5.24 |
| MnO | 0.07 |
| $TiO_2$ | 0.21 |
| $P_2O_5$ | 0.04 |
| LOI[b] | 6.77 |
| $SO_3$ | 11.25 |
| Sum | 100.9 |
| $CO_2$[c] | 0.62 |

[a] The elements are given in terms of the corresponding oxides, percent of sample

[b] LOI = Loss on ignition

[c] $CO_2$ is already included in LOI

Table 6 Phase composition[a]

| | |
|---|---|
| CaO | 1.1 |
| $Ca(OH)_2$ | 19.4 |
| $CaCO_3$ | 1.4 |
| $CaSO_4$ | 19.1 |
| Gehlenite | 3.0 |
| Larnite | 9.0 |
| Ferrite | 8.0 |
| Quartz | 30.0 |
| Iron oxides | 0.4 |
| Others, nonspecified | 5.4 |
| $LOI_{corr}$[b] | 1.4 |
| Sum | 98.2 |

[a] According to the calculations described in the text, percent of sample

[b] "$LOI_{corr}$" is the loss on ignition less the $H_2O$ corresponding to $Ca(OH)_2$ and the $CO_2$ corresponding to $CaCO_3$