

electrodes and synchronising their dropping times. On the other hand, rising electrodes are easily duplicated and provision can readily be made for running twin electrodes off the same timing circuit.

A further advantage of the new system is that the cells can be constructed from a wide variety of materials, chosen to suit particular needs, e.g., a polythene cell for use with hydrofluoric acid solutions.

Finally the electrode has distinct advantages in possible applications to plant control and continuous analysis, in that blockages are impossible and synchronisation with the sweep potential is automatic.

Acknowledgment

Grateful acknowledgment is made to Mr. R. J. Weir, who designed and built the timing circuit and who made many useful suggestions.

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Received 15 February, 1960

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AN X-RAY STUDY OF PULVERISED FUEL ASH

By (the late) H. S. SIMONS and J. W. JEFFERY

Pulverised fuel ash has been subjected to X-ray examination and chemical analysis and the main mineralogical and physical characteristics have been determined. It is shown that the ash is a very complex material in which the overall chemical composition varies from particle to particle.

It is tentatively concluded that there is a positive correlation between pozzolanic activity and glass content. The types of combination of iron present in the ash have been determined and the effect of hydration examined.

Introduction

The increasing use of pulverised coal for firing generating station boilers has led to the problem of the disposal of millions of tons of pulverised fuel (p.f.) ash. This ash is produced from the particles of coal, which pass through the furnace with the air stream, burning as they go, and ending as particles of more-or-less fused ash which pass out with the flue gases and are collected in the electrostatic precipitator. There is little contact between particles in the furnace so that their composition depends on the mineral content of the original coal particle, which may be very different from the bulk mineral composition. Often the ash is fused and the particle then ends as a smooth sphere which is frequently hollow ('cenosphere'). In addition, the short time in the combustion chamber may not be sufficient to produce equilibrium conditions in many particles and the final composition of the particle would thus not be its equilibrium composition. In particular, some of the constituents may be present as glass without any well-defined composition. For these reasons the characterisation of the ash is a difficult problem, requiring a combination of methods, and particularly the use of X-ray methods, for its solution. The investigation to be described was largely concerned with the application of X-ray methods to this problem, and as far as possible the characterisation of p.f. ash was correlated with its utilisation for various purposes, since the primary object of the characterisation was to help in finding economic uses for the material.

Preliminary investigations showed that the material is very variable, with a mineralogical

composition bearing little relation to the chemical analysis, and contains a large number of minor constituents. It became necessary to improve the X-ray techniques and re-photograph most of the specimens, both of p.f. ash and of the samples of various known substances which might conceivably be present as minor constituents. Altogether some 900 powder patterns were obtained from several hundred specimens.

Experimental

Materials used

Pulverised fuel ash

A large number of p.f. ash samples was investigated, either to check the variability of the ash and correlate its properties with the conditions of its production, or to investigate samples which were already the object of some other investigation connected with the use of the ash. A detailed list of these samples is given in the Appendix.

Coal

Samples of coal from the bunkers of three generating stations were investigated, with an attempt in one case to correlate with results for an ash [sample (b)].

Standard minerals

Nearly 150 samples of minerals (including all those finally identified) which might, from the chemical composition, exist in p.f. ash, either dry or hydrated, were obtained from various sources.

Methods of investigation

The samples were investigated as received and after various physical and chemical treatments as detailed in the appropriate sections. They were investigated optically under the polarising microscope and by X-ray powder photography, using a 9-cm. Debye-Scherrer camera for the earlier work and for the later work a Nonius Guinier focusing camera having a dispersion equivalent to a 22.97-cm. Debye-Scherrer camera but with much better resolution because of the sharply focused lines. Although the determination of the many phases present could not have been achieved without this camera, its use brought with it a number of problems. Exposure times were 4–8 times as long, but as four specimens can be photographed together and an exposure taken overnight, this finally increased the number of specimens which could be dealt with per day rather than otherwise. The main difficulty lay in utilising the A.S.T.M. X-ray Powder Data File for identification. So many doublets are resolved which would appear as single lines in the File that in its present form the latter is of little direct use. The information in the file itself is useful for checking purposes on occasion, but most of the identification of the minor constituents was done by comparison with the library of standard photographs built up during the course of the investigation.

Single particles of ash were photographed using the microcamera¹ and the Ehrenberg-Spear fine-focus X-ray tube.

In the later stages of the investigation the Geiger counter diffractometer was used to obtain quantitative measurements of the main crystalline phases. Calibration curves were obtained of the ratio of integrated line intensities against composition for mixtures of each of the pure phases with an internal standard. The samples of ash were mixed with a known proportion of the standard and the selected lines of the various phases and the standard measured. The ratios of intensity, in conjunction with the calibration curves, then gave the amounts of the different phases present in the sample.

Integrated intensities were measured using step-by-step counting and measurement of the area under the plotted curve. For most of the measurements this was done with a print-out counter and automatic stepping-on equipment.

Glass was measured by difference.

Results

Chemical and mineralogical composition

From the analysis of ignited ash from over 20 different stations the range of chemical composition (% by weight) is as follows: SiO₂, 35–51; Al₂O₃, 21–30; Fe₂O₃, 5–27; CaO, 2–9.

The total of other constituents rarely exceeds 5%. In the ash as produced, carbon is always present, but where combustion in the furnace is satisfactory it should be less than 5%. In exceptional cases it may rise to 20% or more and when present to more than about 10% it may be deleterious, as, for example, in the use of p.f. ash as a cement substitute in mass concrete. However, in brickmaking and in the preparation of sintered aggregate the combustion of the carbon provides part of the heat required in the process.

The mineralogical composition of 12 ashes (source, see Table I) including the total of crystalline components is given in Table IIa. Table IIb gives the proportion of glass and its chemical composition calculated by difference for those nine ashes for which full chemical analysis was available. The proportion of glass is in every case greater than 50% and goes up to nearly 90%.

Quartz (SiO_2) and mullite ($2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$) are the main crystalline constituents of most British ashes, but in the American ashes studied the iron oxides magnetite (Fe_3O_4) and haematite (Fe_2O_3) occurred in nearly as large proportions.

The range of quantitative measurements for British ashes is: quartz (1–6.5%); mullite (9–35%); magnetite and haematite (5% or less). For American ashes the proportions are: quartz (0–4%); mullite (0–16%); magnetite (0–30%); haematite (1–8%). The chemical composition of the glass phase is perhaps slightly less variable. The range of the main components for all nine ashes is: SiO_2 , 47–65%; Al_2O_3 , 8–34%; Fe_2O_3 , 4–15%; CaO , 1–10%; $(\text{Na},\text{K})\text{O}$, 0–7%; MgO , 0–4%; SO_3^{2-} , 0–3%. Minor mineral components identified are: lime (CaO); anhydrite (CaSO_4); gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); dicalcium ferrite ($2\text{CaO} \cdot \text{Fe}_2\text{O}_3$); and in wet conditions, ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$). Anatase (TiO_2) and γ -alumina (Al_2O_3) have been less certainly identified in a few cases. The ash from the Russian lignite-burning station at Komlo contained no mullite and, besides quartz and haematite, contained some mica.

Three samples of coal were examined as a preliminary to a programme of investigation of coal and ash from a number of selected stations. The programme was later abandoned and the only result was a qualitative determination of the mineral constituents of the three coal samples. The minerals found were: quartz, kaolin minerals, montmorillonite, mica minerals and pyrites, in varying proportions.

A preliminary examination was made of deposits from p.f. turbine blades. As the X-ray photographs showed this material to be very complex and to have no obvious relation to fly ash, no further attempt was made to identify the components.

Physical characteristics

Microscopical examination.—Microscopical examination (and determinations of free-falling terminal velocity made at the Central Electricity Research Laboratories) showed that the p.f. ash contained particles ranging from less than 1μ to about 120μ in dimensions; exceptionally, particles as large as 500μ occur in such ash.

These results, and others on form, colour and texture, agree with the more detailed particle examination of p.f. and other ashes by Crossley.²

Table I

Sample no.	Power station or area of origin	Description of p.f. ashes studied	Notes
PJ/189*	Braehead P.S.		Corresponding to coal from the Scottish field
PJ/190	Brunswick Wharf P.S.		Corresponding to coal from the East Midlands field
PJ/191	Dunston P.S.		Corresponding to coal from the Northumberland and Durham field
PJ/192	Llynfi P.S.		Corresponding to coal from the South Wales field
PJ/194	North Wilford P.S. Boiler No. 16		Produced in low temperature combustion chamber
1	Chicago		From Prof. Marshall (Glasgow University)
2	Source confidential		From the Ready Mixed Concrete Ass., Washington (Lot 2448)
3	Chicago		From the Bureau of Reclamation, U.S. Dept. of the Interior
4	Argo, Illinois		
5	Baltimore, Maryland		
6	Cumberland, Maryland		
7	Philadelphia, Penn.		From G. & W. H. Corson Inc., Plymouth Meeting, Pa.

* The PJ numbers are Central Electricity Research Laboratory (C.E.R.L.) reference numbers.

X-ray examination of single particles and separated fractions.—X-ray photographs of stationary individual white particles gave smooth powder rings of quartz and mullite. In only one case could slight spottiness of the quartz rings be detected. These results indicate inter-growth of very small crystals of quartz and mullite in each particle and this is borne out by the fact that in a centrifugal separation the mullite (and a considerable proportion of the iron oxides) appeared in the light fraction although its density is greater than that of the liquid used. Some of the iron oxide fraction appears to be less mixed with other minerals, most of the heavy fraction being magnetite and haematite.

Veloduct grading (air elutriation) produced no separation of the constituents nor did grinding produce any detectable alteration in properties.

Correlation of physical and chemical properties with pozzolanic activity.

A pozzolana may be defined as a material which is capable of reacting with lime in the presence of water at ordinary temperatures to produce cementitious compounds.³ Such a substance may be used to replace a proportion of Portland cement, reacting with the free lime produced on hydration. P.f. ash possesses such properties to some extent and was first used as a partial substitute for cement (up to 25%) in mass concrete structures in the U.S. and subsequently in this country. In the U.S. it was reported that p.f. ashes differ considerably in pozzolanic properties and that Chicago ash was particularly good. A number of British ashes (Table I) were examined for pozzolanic properties (see Table IIa) by the Cement & Concrete Ass. (CACA) and part of the sample was submitted for X-ray examination. A number of ashes (Table I) were also obtained from the U.S.A. which had been tested for pozzolanic properties and characterised as 'good' or 'bad'.

The results of the quantitative X-ray examination are given in Tables IIa and IIb, together with an indication of the pozzolanic properties. Although contradictory results exist on the

Table IIa

Mineralogical composition of crystalline fraction (% by wt.) and relation to pozzolanic properties

Sample	Quartz	Mullite	Magnetite	Haematite	Other cryst. components	Carbon	% of total less carbon	Pozzolanic properties*
PJ/189	6.5	35	5	<1	<1	2	48	68
PJ/190	4.5	13	3	<1	<3	3	22	74
PJ/191	4	22	<1	<1	<3	4	29	—
PJ/192	1	9	<1	<1	<1	20	13	61
PJ/194	6	26	<1	<1	<5	3	34	70
1	1	3	3	5	<5	<1	16	Good
2	4	12	5	3	<1	5	25.5	Good
3	1	<1	9	4	<2	2	17	Good
4	<1	5	30	7	<1	6	47	Poor
5	3	3	4	8	<2	14	20.5	Poor
6	4	16	<1	1	<1	19	27	Poor
7	2	6	18	7	<1	5	36	Good

Table IIb

Chemical composition of glass fraction (% by wt.) and relation to pozzolanic properties

Sample	% of glass	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	(Na,K)O	MgO	SO ₃ ²⁻	Pozzolanic properties*
PJ/189	52	64.5	12	6	10	3	4	1	68
PJ/190	78	51	22.5	8	7.5	7	2	2	74
PJ/191	71	53	16	15	9	4	2.5	1	—
PJ/192	87	60.5	22.5	4.5	5.5	6	0.5	0.5	61
PJ/194	66	51	8	15	14	6.5	4	1.5	70
2	74.5	60	28	10	1.5	0	0.5	0	Good
5	79.5	47.5	34	10	7.5	0	1	0.5	Poor
6	73	59.5	23.5	10	1.5	3.5	0.5	0.5	Poor
7	64	51.5	26	1.5	13	2.5	2.5	2.5	Good

*% of strength after 28 days of a mix in which 25% of the cement was replaced by p.f. ash, compared with the strength of the corresponding plain concrete (Cement and Concrete Ass., unpublished Tech. Rep. No. TRA/163)

effect of carbon content on the strength of concrete containing fly-ash, the limit specified for use as a cement substitute in the United States has been 12%. It would appear necessary, therefore, to ignore results for ashes with more than 12% carbon content. In that case the few remaining results are not inconsistent with a positive correlation between pozzolanic activity and glass content.

This very tentative conclusion is supported by tests carried out by the U.S. Corps of Engineers on four samples (not available here), including a microscopical examination for glass.⁴ The greater the proportion of glass the greater was the compressive strength in test cubes containing ash admixture. No other correlation is apparent and the accuracy of the figures does not justify any elaborate statistical analysis. The total number of samples in all the investigations is small and in the case of the British ashes the differences in compressive strengths are of doubtful significance. It is clear that there are differences in pozzolanic properties between different ashes, that excessive carbon content leads to low strength, and that high glass content may be advantageous, but the main conclusion which can be drawn from the experimental evidence is that no p.f. ash is a satisfactory substitute for cement where high early strength is necessary. Even the best ash, used as a 25% replacement for cement (the minimum substitution likely to be economic), will normally only give about 75% of the strength given by unadulterated cement in the early stages (up to 28 days) and about a year's ageing is required before such p.f. ash concrete is as strong as that made with a normal mix. Thus its use is restricted in the main to mass concrete structures and in these it may have the added advantage of producing heat from the hydration reaction more slowly and thus reducing the problem of heat dissipation. It can also be used for prefabricated blocks, when storage over the necessary period can be arranged, or more especially with steam curing, which gives such blocks even greater immediate strength than those made with normal cement.

The ultimate strengths of concrete made with different ashes are not significantly different provided the carbon content is not too high, and the differences at early ages are all normally much less than the difference between concrete containing p.f. ash and that made with normal cement. However, occasionally a sample gives high early and ultimate strengths for reasons which are still not properly understood. Further investigation might, therefore, still produce useful results.

The iron content of p.f. ash

The detailed investigation of the iron content of p.f. ash was undertaken in conjunction with work at C.E.R.L. on the feasibility of producing a magnetically concentrated material suitable for use as iron ore.

Separation of iron compounds.—Iron occurs in p.f. ash as crystalline components (mainly magnetite and haematite) and as glass. X-ray photographs of the fractions from magnetic separation of p.f. ash show that the magnetic fraction contains not only most of the magnetite, but also almost as high a proportion of the weakly magnetic haematite and a considerable proportion of the non-ferrous minerals. This is true both for dry and wet separation, although wet separation is more effective.

The poor separation is due to the intimate intergrowth of magnetite and haematite, the mixture of iron and other minerals in the same particle, the sintering together of several particles to form clumps, and the combination of iron with alumina and silica in the glass.

In the case of heavy-liquid separation using iodoform (sp. gr. 2.9) the photograph of the heavy fraction showed strongly the combined patterns of magnetite and haematite, but only very faint lines of the silicate minerals. The light fraction, on the other hand, gave a photograph showing considerable quantities of the iron minerals as well as most of the quartz and mullite. This shows that some of the iron oxide occurs more or less free from silicate material.

Prolonged grinding makes little difference to the efficiency of the separation in either case.

It is clear that economic separation of iron oxides from p.f. ash on a large scale is not likely to be easily achieved, although it may be possible to produce a concentrated fraction. If separation can be achieved at all it may be more feasible to separate the pyrites from coal before its valuable sulphur content is lost. Some of the pyrites is so finely disseminated that it can hardly be separated, but some occurs in more concentrated form and might be extracted from the pulverised fuel by electrostatic separation. It is presumably this more concentrated pyrites which gives rise to the comparatively uncontaminated iron oxides.

Oxidation of pyrites and detection of maghemite ($\gamma\text{-Fe}_2\text{O}_3$).—The oxidation of pyrites produces first magnetite (Fe_3O_4) and then, under certain conditions, maghemite, which has a defect spinel structure related to magnetite. It is very unlikely that this form of ferric oxide would be produced under furnace conditions, but as some microscopical observations on the change of colour of p.f. ash particles on roasting had been interpreted as indicating the presence of maghemite, it was important to be certain on this point. The maghemite powder pattern is very similar to that of magnetite and in small proportions maghemite can only be detected by a slight difference in high angle spacings. However, the resolution of the Nonius powder camera is sufficient to make the distinction unequivocally and in no case has maghemite been detected in p.f. ash.

The relative proportions of magnetite and haematite ($\alpha\text{-Fe}_2\text{O}_3$) depend on the oxidising conditions in the furnace and both oxides are usually present as an intimate intergrowth in p.f. ash particles derived from pyrites. Roasting p.f. ash always increases the proportion of haematite.

Types of iron compound present in p.f. ash.—Jackson & Lowe,⁵ from chemical and microscopical studies of a high-iron p.f. ash (PJ/292) and magnetic concentrates therefrom, differentiated four types of chemical combination of iron provisionally termed 'soluble,' 'non-magnetic,' 'magnetic,' and 'silicate' iron (samples 1–3 in Table III). X-ray examination of these samples has been made and also of residues obtained by extraction of another sample of the ash with HCl of different concentrations (samples 4–6 in Table III). The X-ray results and the chemical analyses of the samples are set out in Table III. No attempt has been made to obtain accurate quantitative results, but the following estimates can be made from the X-ray photographs:

(i) All the samples except no. 6 have considerable quantities (of the order of 20% or more) of combined haematite and magnetite.

(ii) Sample 2 (Run 6) and Sample 3 (Run 12) both have considerably higher proportions of magnetite and haematite than Sample 1, and Sample 2 has the highest proportion.

(iii) All the samples except nos. 5 and 6 have small amounts (a few %) of dicalcium ferrite; nos. 1 and 4 having about the same quantity, followed by nos. 3 and 2 in order.

(iv) The amounts of lime and anhydrite present in samples 1–3 are very small—not much more than 1%.

No iron compound could be identified corresponding to the 'soluble' iron. This is not surprising since the chemical evidence shows that it is present to less than 1%, i.e., below the

Table III

Results of chemical analysis and X-ray investigation of a high-iron p.f. ash, magnetic concentrates prepared from it, and residues from HCl extraction of another p.f. ash

Sample no.	1	2	3	4	5	6
Description	Original ash	Magnetic concentrate Run 6	Run 12	Second sample treated with HCl 0.02N ^a	0.2N ^b	5.0N ^c
<i>Chemical analysis*</i> (% Fe_2O_3 of air-dried sample)						
Total	23.1	67.9	50.8	22.3	17.3	4.3
'Silicate' iron	3.9	0.7	1.3	4.3	4.3	4.3
'Magnetic' iron	13.1	64.0	44.3	13.0	13.0	—
'Non-magnetic' iron	5.8	2.5	4.3	5.0	—	—
'Soluble' iron	0.3	0.7	0.9	—	—	—
<i>X-ray analyses</i>						
Quartz, SiO_2	+	+	+	+	+	+
Mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	+	+	+	+	+	+
Haematite, $\alpha\text{-Fe}_2\text{O}_3$	+	+	+	+	+	—
Magnetite, Fe_3O_4	+	+	+	+	+	—
$2\text{CaO} \cdot \text{Fe}_2\text{O}_3$	+	+	+	+	—	—
Anhydrite, CaSO_4	+	+	+	—	—	—
Lime, CaO	+	+	+	—	—	—

+ = present - = absent

* Analyses and chemical preparation by Jackson & Lowe⁵

^a 0.76% Fe_2O_3 dissolved in 15 min.

^b 5.77% Fe_2O_3 dissolved in 15 min.

^c 18.8% Fe_2O_3 dissolved in 60 min.

limit for most X-ray identification. However, CaSO_4 is shown to be dissolved by 0.02N-HCl, and iron sulphate, if it is present as suggested by Jackson & Lowe,⁵ would also be expected to be extracted.

The main constituent (and the only one identified by X-rays) of the 'non-magnetic' iron is dicalcium ferrite ($2\text{CaO}, \text{Fe}_2\text{O}_3$) and the quantity estimated from the photographs is consistent with the chemical evidence. The brown colour of $2\text{CaO}, \text{Fe}_2\text{O}_3$ strengthens the microscopical identification of brown particles as belonging to this fraction.⁵

The 'magnetic' iron consists of both magnetite and haematite. The amounts of these two oxides indicated by the X-ray photographs are again consistent with the chemical results. The presence of haematite explains the fact that ferrous iron is present in Sample 1 only to the extent of 14.5% of the 'magnetic' fraction instead of the 31% which would be the case if it were all magnetite ($\text{FeO}, \text{Fe}_2\text{O}_3$).⁵

The 'silicate' iron was not identified by X-rays although in the case of Samples 1, 4, 5, and 6, the amount should have been large enough if present as a single, well-crystallised compound. The X-ray evidence supports the microscopical identification of glassy particles⁵ as belonging to this fraction.

The combined chemical⁵ and X-ray evidence supports, or is consistent with, the following identification of the four iron fractions in p.f. ash PJ/292:

- 'Soluble' iron—iron sulphate, <1%
- 'Non-magnetic' iron—dicalcium ferrite ($2\text{CaO}, \text{Fe}_2\text{O}_3$), ~5%
- 'Magnetic' iron—magnetite (Fe_3O_4) and haematite (Fe_2O_3), ~20%
- 'Silicate' iron—glass, ~4% from chemical evidence only

Effects of hydration

Consolidation of wet dumps.—Ettringite was first identified in p.f. ash from Early G.S. dump which had been in a wet condition for about 2 years [sample (g)]. Later, ash from three generating stations [sample (l)] was examined before and after hydration under water for one month. The main difference in the X-ray photographs was the appearance of the pattern of ettringite and the weakening or disappearance of the patterns of gypsum and anhydrite in the hydrated samples.

It is known that p.f. ash changes in plasticity during hydration. Nurse⁶ suggested that the first effect is the hydration of anhydrite to gypsum, causing a stiffening similar to the setting of ordinary plaster. Secondly, the rehydration of some of the ash to form clay-like minerals might cause the rise in the plasticity index sometimes noted after 28 days. This latter reaction would, of course, tend to oppose the consolidation of dumps although its effect might only be noticeable when the crystals responsible for the setting tendency were broken up, as in the working of the raw materials for brick making under much wetter conditions than are normally present in dumps.

The fact that moist dumps tend to consolidate is probably due mainly to the formation of ettringite, although the formation of calcium silicate hydrates from the glassy fraction of the ash cannot be ruled out, since it is extremely difficult to detect this material and quite large amounts might be present without giving any X-ray pattern.

Effects of p.f. ash constituents on plant growth.—Dr. W. J. Rees of the Department of Botany, Birmingham University, supplied six samples of p.f. ash on which plant-growth investigations were in progress. The determination of the source of soluble alumina and methods for its fixation were the main objects of the X-ray investigation. The specimens were examined (a) as received; (b) after 1 month under water; (c) after 1 month under lime water. The results are given in Table IV. The content of ettringite is given in terms of the strength of the main diffraction line at 9.80Å. For tetra-calcium aluminate hydrate (C_4Aaq) the strength of the 8.0Å line is given. This compound was only observed after treatment with lime water.

The development of ettringite and C_4Aaq in lime water suspensions shows the presence of soluble alumina, presumably from the glass phase of the ash. It also shows that the alumina can be at least partially fixed by the addition of lime. The ratio of ettringite to C_4Aaq probably depends on the amount of sulphate present in the ash, but as the amounts of ash and lime water were uncontrolled the quantitative results are not very significant. On dumps the carbon dioxide of the atmosphere would be expected to turn the C_4Aaq into the carbo-aluminate—the carbonate analogue of ettringite.

Table IV
Content of ettringite and C₄Aaq and biological effects
 Generating station

Compound and specimen treatment	Generating station					
	Hams Hall	Wigan	Meaford	Connah's Quay	Llynfi	Poole
Ettringite (a)	nil	v. weak	nil	nil	nil	nil
Ettringite (b)	nil	weak	v. v. weak	nil	nil	nil
Ettringite (c)	medium	weak	v. weak	v. weak	nil	weak
C ₄ Aaq (c)	weak	v. v. weak	weak	weak	v. weak	weak*
Plant response	poor	poor	fair	fair	good	good

* Slightly different spacing indicating formation of the alternative form of C₄Aaq.

Quartz content of p.f. ash used in brickmaking

The possibility that there might be a danger of silicosis in handling p.f. ash for brickmaking led to an investigation by the Government Chemist of the quantity of 'hard, free silica' present in ash from six generating stations. Ash from the same stations and probably, though not certainly, from the same bulk samples, was analysed quantitatively for quartz using the Geiger counter diffractometer. The results are given in Table V. The relatively large error in the quartz determinations is due mainly to the high background count and the consequent uncertainty of the background level. It is also partly due to statistical inaccuracy, as these results were obtained without automatic counting equipment and the number of counts was insufficient to eliminate errors from this source.

Conclusions

A better understanding of many of the properties of p.f. ash has been obtained as a result of the application of X-ray methods in conjunction with many other forms of investigation, ranging from experiments on plant development for the consolidation of dumps to the determination of pozzolanic properties of p.f. ash used as a substitute for cement. The main mineralogical and physical characteristics of the ash have been determined, but it has been shown to be such a complex material that its characterisation in detail would be extremely difficult. Not only does the overall chemical composition vary from particle to particle, but the amount and composition of glass and the mineral composition of the crystalline fraction bears little relation to the equilibrium products, and this also varies from particle to particle.

It may be that future uses may be found for p.f. ash which require more detailed characterisation, or may arise from it, but at present the possibilities do not seem to warrant the considerable scientific effort which would be necessary for its achievement.

Acknowledgments

The major part of the work described in this paper was carried out by the late Dr. H. S. Simons, whose untimely death robbed the final stages of the investigation of the benefit of his wide experience and unrivalled knowledge of the fields of X-ray powder analysis and industrial application of materials. While he drew many of the conclusions from the experimental results, the actual presentation is the responsibility of the surviving author, who wishes to thank Prof. J. D. Bernal for his constant encouragement and advice; Dr. R. W. Nurse, of the Building Research Station, for many helpful discussions and practical assistance; Dr. J. Forrest and the

Table V
Quartz content of p.f. ash used in brickmaking
 % by weight

Specimen number	Generating station	% by weight	
		'Hard, free silica'	Quartz
1	Braehead	4.9	4.5 ± 2.0
2	Brunswick Wharf	4.3	4.0 "
3	Dunston	4.6	3.5 "
4	Llynfi	3.2	5.0 "
5	N. Wilford	6.4	6.0 "
6	Stourport	2.5	2.5 "

staff of the Central Electricity Research Laboratories, and Mr. R. Ll. Rees and his staff for their collaboration; and the Electricity Supply Research Council for sponsoring the investigation and granting permission for publication of the results.

Appendix

Samples of p.f. ash

- (a) A series of chemically analysed ashes supplied by the C.E.R.L.
- (b) A series of samples from two London power stations, some taken on consecutive days and others over a longer period.
- (c) A series of samples corresponding to coal from the Scottish, East Midlands, Northumberland and Durham, and South Wales coal fields.
- (d) Samples from low- and high-temperature furnaces.
- (e) A series of samples obtained from the United States chosen for good and bad pozzolanic properties.
- (f) Four samples from a Russian (Komlo) generating station burning lignite.
- (g) P.f. fresh and aged ash, used in making lightweight cement blocks (from John Laing).
- (h) Samples with high CaO content (from C.E.R.L.).
- (i) Samples with high iron content and enriched by magnetic separation (from C.E.R.L.).
- (j) Samples with high iron content roasted in air for 66 hours (from C.E.R.L.).
- (k) Residues from acid attack of (i) (from C.E.R.L.).
- (l) Ash from three power stations: (i) kept dry; (ii) kept under water for 1 month.
- (m) Six samples of p.f. ash from dumps on which botanical investigations were being undertaken by Dr. W. J. Rees of Birmingham University.
- (n) Samples of ashes used in brickmaking—for quartz determination in connexion with a possible silicosis danger.
- (o) Samples of deposits from p.f. turbine blades.

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Received 26 January, 1960;
amended manuscript 30 March, 1960

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KINETICS OF OXIDATION OF COAL. II.* COMPARISON OF THE REACTIVITIES OF FOUR COALS

By T. WOOD

An attempt has been made to measure the reactivities of four coals using the Warburg technique. Temperature is shown to be a significant factor; the precision of the method is insufficient to determine the influence of particle size. The method would be well suited for a large-scale statistical survey to investigate the influence of pyrites, or any other constituent, on the reactivity of a coal.

Introduction

This work was part of a project, undertaken on behalf of the Joint Coal Board of New South Wales, to investigate the problem of spontaneous combustion in the Greta coal seam. Because of spontaneous combustion, some mines in this area are forced to seal off large amounts of good-quality gas coal. As other mines in the same region are comparatively free from spontaneous combustion, it was suggested that there might be some difference in the chemical reactivities of the coals in various parts of the seam. In particular, it is a strong opinion of the mining engineers in the district that the pyritic content of the coal is responsible for the different behaviour. The available evidence from previous work does not support this view.¹

* Part I: *J. appl. Chem.*, 1958, **8**, 565.