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Content of clinker and other materials in personal thoracic aerosol samples from cement plants estimated by scanning electron microscopy and energy-dispersive X-ray microanalysis

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Abstract

Objectives. To estimate the composition and exposure to clinker and other specific components in personal thoracic dust samples of cement production workers.

Methods. A procedure for the classification of airborne particles in cement production plants was developed based on classification trees. For this purpose, the chemical compositions of 27,217 particles in 29 material samples (clinker, limestone, gypsum, clay, quartz, bauxite, iron source, coal fly ash, and coal) were determined automatically by scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDX). The concentrations of the major elements in cement (calcium, aluminium, silicon, iron, and sulphur) were used for the classifications. The split criteria of the classification trees obtained in the material samples were used to classify 44,176 particles in 34 personal thoracic aerosol samples. The contents of clinker and other materials were estimated, and the clinker contents were analysed statistically for differences between job types and job tasks.

Results. Between 64% and 88% of the particles from material samples were classified as actual materials. The material types with variable composition (clay, coal fly ash, and coal) were classified with the lowest consistency (64% to 67%), while materials with a more limited compositional variation (clinker, gypsum, and quartz) were classified more consistently (76% to 85%). The arithmetic mean (AM) of the clinker content in personal samples was 62.1%, the median was 55.3%, and 95% confidence interval (CI) was 42.6% to 68.1%. No significant differences were observed between job types. However, the clinker content in samples when workers handled materials with high clinker content was significantly higher than when materials with lower clinker content were handled, 85% versus 65% ($P = 0.02$). The limestone content was AM 14.8%, median 13.2% (95% CI 5.5 to 20.9), whereas the other materials were present with relative abundances of median ≤ 6.4%.

Discussion. Automated particle analysis by SEM-EDX followed by classification tree analysis quantified clinker with fairly high consistency when evaluated together with raw materials that are expected to be airborne in cement production plants. The clinker proportions for job types were similar. Tasks *a priori* ranked by assumed clinker content were significantly different and according to expectations, which supports the validity of the chosen methodology.

Conclusions. The composition of personal samples of mineral aerosols in the cement production industry could be estimated by automated single particle analysis with SEM-EDX and classification by a classification tree procedure. Clinker was the major component in the thoracic aerosol that cement production workers were exposed to. Differences between job types were relatively small and not significant. The clinker content from tasks was in agreement with assumptions.

Key words: cement industry; classification tree; particle classification; thoracic dust composition.

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What's Important About This Paper?

Aerosol exposure in cement production plants is associated with negative respiratory effects including airway symptoms and lung function decline, which are believed to be caused by clinker. This study employs a classification algorithm to estimate the content of clinker and other raw materials used in cement production in thoracic aerosol samples. The method resulted in lower clinker estimates than in previous studies. Correct estimates are important for exposure-response analyses.

Introduction

Exposure to dust in cement production is associated with several adverse health effects including pneumoconiosis, rhinitis, emphysema, asthma, bronchitis, and lung function decline (Health and Safety Executive 1994, 2005). A clear exposure-response relationship between lung function decline and exposure to the thoracic aerosol fraction was found in a large longitudinal study of cement production workers in Europe and Turkey (Nordby et al. 2011, 2016; Notø et al. 2015).

Portland cement is the most common type of hydraulic binder in the construction industry. It is composed of clinker and gypsum, 95% and 5%, respectively (CEN 2011; Taylor 2004). Other additives with cementitious properties can be mixed with clinker to different types of blended cement. Clinker is produced from a variety of raw materials like limestone, clay, quartz, gypsum, coal fly ash, and fuels like coal. It contains four main phases, alite, belite, aluminate, and ferrite. Clinker reacts with water and forms a highly alkaline blend with a pH that exceeds 13 (Vollpracht et al. 2016). It is supposed that clinker is the main cause of the observed lung function decline. However, the role of clinker is not clear because quantification of clinker exposure has not yet been performed in epidemiological studies of cement production workers.

Cement production workers are not only exposed to clinker particles but also to a variety of raw materials. To date, only a few detailed studies have been carried out on individual components of workplace aerosol in cement production plants. These studies reported exposure to quarts (Abrons et al. 1988; Fell et al. 2003; Mwaiselage et al. 2006; Mirzaee et al. 2008; Zeleke et al. 2011). There is, to the best of our knowledge, only one published study investigating the presence of clinker particles at cement workplaces by electron microscopy (Ervik et al. 2022).

Quantification of clinker in workplace aerosol is an analytical challenge. Hahn et al. (1998) reported cement exposure in different cement industries using selectively extracted silicon as a marker of cement. Silicon was extracted with maleic acid dissolved in methanol and detected by total reflection X-ray fluorescence analysis. As this method dissolves other silicon-containing components used in cement, such as blast furnace slag, oil shale, coal fly ash, and trass (Institut für Gefahrstoff-Forschung der Bergbau-Berufsgenossenschaft (IGF) 1994), clinker exposure in the production of blended cement will be overestimated. This is even likely when these components are used as raw materials in the production of Portland cement. Peters et al. (2009) estimated cement by quantifying calcium in aerosol samples assuming that clinker was the only source of calcium. This method is likely to overestimate cement in the construction industry because materials that are mixed with cement to form concrete may contain calcium as well. In cement production plants, this systematic overestimation is worse because the calcium content in essential raw materials such as limestone and gypsum is substantial (40% and 23% by mass, respectively). X-ray diffraction (XRD) analysis is routinely used to measure the phase composition of clinker and cement in material samples (Stutzman et al. 2016; Mukhopadhyay et al. 2019). However, no publications on the determination of clinker by XRD in personal samples have been found. Recently, Weinbruch et al. (2023) determined the composition of a large number of personal thoracic samples that had been analysed by inductively coupled plasma optical emission spectrometry separately for water—and acid-soluble fractions by positive matrix factorization. The clinker fraction could be estimated from the identified factors, which allows for further epidemiological analyses of respiratory effects in the study where the samples were collected (Nordby et al. 2016). In the present study, we characterize workplace dust in cement plants by scanning electron microscopy and energy-dispersive X-ray microanalysis (SEM-EDX) as described by others (Skogstad et al. 1999; Willis et al. 2002; Hammer et al. 2019). The samples were collected simultaneously with the samples for the study by Notø et al. (2016), a subset of the large prospective exposure study of European cement production workers (Notø et al. 2015). One of the plants was studied earlier using SEM-EDX (Ervik et al. 2022). As different particle classification procedures were applied in the two studies (classification based on chemical boundary conditions of minerals by Ervik et al. (2022)

versus classification trees obtained on raw materials in the present contribution), the results for this plant can be used to check the consistency of both approaches. In addition, our study will enlarge the knowledge of particle exposure in cement production significantly.

Methods

Samples

Material samples were obtained from four cement production plants and consisted of milled limestone, clay, quartz, bauxite, iron source, coal fly ash, coal, gypsum, and clinker.

Personal exposure measurements were performed in 12 cement production plants located in Norway, Sweden, Estonia, Switzerland, Greece, and Turkey, all members of the European Cement Association (CEMBUREAU, Brussels, Belgium). The samples are a subset of a much larger epidemiological study of lung function decline in the cement production industry in Europe and Turkey (Notø et al. 2015; Nordby et al. 2016). Only samples with low particle density were selected due to requirements from the SEM-EDX analysis.

Thoracic aerosol samples were collected in the breathing zone during a work shift using GK 2.69 cyclones (BGI Instruments, Waltham, MA, USA) at a flow rate of 1.6 L/min maintained by portable pulsation-free pumps (NIOH, Oslo, Norway). Particles were collected on 37 mm diameter polycarbonate (PC) filters with 0.8 µm pore size (Millipore, Cork, Ireland) mounted in 3-piece cassettes that fit onto the 37 mm GK 2.69 sampler (Millipore Corp., Bedford, MA, USA).

Gravimetry

The aerosol mass in personal samples was determined with an MC5 microbalance (Sartorius AG, Göttingen, Germany) at 20°C ± 1°C and 40% ± 2% relative humidity. Further details can be found elsewhere (Notø et al. 2016). The LOD and LOQ for the PC filters were 0.013 and 0.043 mg, respectively.

Scanning electron microscopy

Sample preparation.

Material samples milled at the cement plants were used as reference materials. The fine fraction of these samples was obtained by (1) pouring the sample on a clean aluminium plate, (2) shaking surplus material from the plate, (3) aerosolization of the adhering particles from the plate onto a polycarbonate filter with 0.8 µm pore size through an aerodynamic deagglomerator fitted in the inlet of a 25 mm diameter Air Monitoring Cassette (Pall Corporation, New York, USA), Fig. 1. These cassettes collect particles evenly distributed on the filter (NIOSH 2019), which facilitates SEM-EDX analysis. The deagglomerator was made of a 4 mm diameter stainless steel tube with a length of 67.5 mm that was compressed to an internal width of 0.6 mm between two parallel rods with a diameter of 6 mm (Fig. 1). A critical flow rate

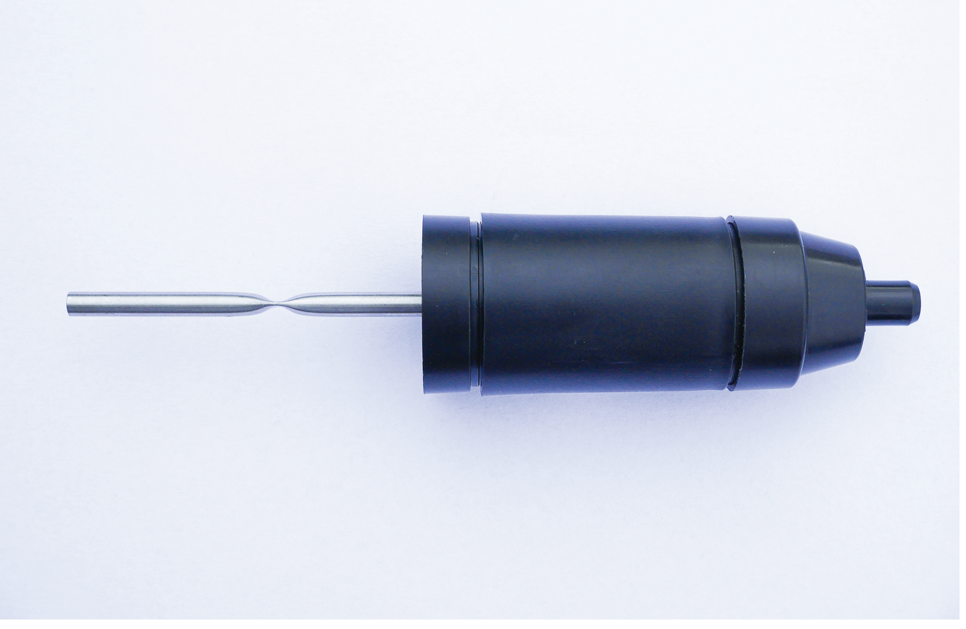

Fig. 1. Aerodynamic deagglomerator fitted in the inlet of a 25 mm diameter air monitoring cassette.

of 2.07 to 2.08 L/min was maintained by a high-volume pump giving a downstream pressure less than half of the upstream pressure. The generated sonic flow conditions through the slit induce shear forces that disperse agglomerates in the aerosol (Cheng et al. 1989). The distribution of particles on the filter was initially judged by observation with an optical microscope at 60× magnification, and sample preparation was repeated if particles were not sufficiently separated. Screened samples were further inspected in SEM to avoid overlapping particles before automated particle analysis with SEM-EDX. Squares of 8 mm × 8 mm were cut from the filter and mounted on 12 mm diameter aluminium pin stubs (Agar Scientific Ltd., Stansted Essex, UK) in a sterile laminar airflow cabinet using double-sided carbon adhesive foil (Agar Scientific Ltd., Stansted, UK). Finally, the samples were coated with approximately 20 nm carbon in a Balzers SDC 050 sputter coater using a carbon thread evaporator CGC 010 system (Balzers, Liechtenstein). The thickness of the carbon layer was controlled by the interference colour on a polished brass stub coated together with the samples (Echlin 2009).

SEM-EDX analysis.

The filter samples were analysed with a field emission scanning electron microscope SU 6600 FESEM (Hitachi, Tokyo, Japan) operated with an acceleration voltage of 15 keV, analytical working distance of 10 mm and electron probe current of 7 to 8 nA (nanoampere). A guard region of 1 mm from the edges was applied during the analysis (NIOSH 2019). Particles were imaged with backscatter electrons (BSE) using a solid-state detector. X-ray spectra of elements with atomic number ≥ 6 (carbon) were recorded with a Quantax 200 microanalysis system (Bruker-AXS Microanalysis GmbH, Berlin, Germany) using an XFlash® 5010 silicon drift detector with an energy resolution of 123 eV (Mn Kα). Automated analysis was performed using the Feature module of the Esprit software (Bruker-AXS Microanalysis GmbH, Berlin, Germany). As a first step in the automatic particle analysis, high contrast (BSE) images were acquired with a resolution of 1,500 × 1,125 pixels (pixel size = 0.10 µm). A minimum particle size to be analysed was defined as an area of 0.2 µm^2. X-ray acquisition per particle was terminated when the sum of X-ray counts from 0.6 to 15 keV reached 25,000 which took on average 100 min/sample. The whole particle except an outer guard band of 2 pixels was scanned during X-ray acquisition. Element concentrations were quantified by the Esprit software using the standard-less peak-to-background ZAF (atomic number Z [Zahl, German], absorption A, and fluorescence F) correction (Goldstein et al. 2018).

In the present study, the so-called geometric effects, i.e. effects resulting from the particle geometry (Goldstein et al. 2018), were not corrected. Neglecting geometric effects may lead to large systematic errors in the measured element concentrations. According to Armstrong (1991), the conventional ZAF correction when applied to particles leads to systematic errors between −50% and +30%. However, significantly lower systematic errors between −15% and +13% were reported by Weinbruch et al. (1997).

Estimation of particle volume and weight in SEM analysis is subject to uncertainty as the particle height and density are not known. However, if particles have similar shapes knowing the exact volume of the particles is not needed when the composition of a sample is to be estimated. Particle volumes (V) were estimated from the equivalent projected diameter (d_{eq}) by $V = (d_{eq})^3$. Particle volume was used as an estimate of particle weight because the materials present in cement production plants have similar densities (2.5 to 3.0 kg/m^3) except for coal (1.4 kg/m^3). The volume of coal particles was multiplied by 0.5 to adjust for the lower particle density. The total volumes of the classified particles were divided by the combined volume of all particles to estimate the weight proportions of the material types.

Particle classification

A classification procedure was used for the classification of particles based on their chemical composition obtained by SEM-EDX. First, a training set of raw materials, clinker, gypsum, and coal was analysed for the construction of classification trees. Then the personal samples were classified using the resulting trees.

Material samples training set.

Classification criteria were developed based on the concentration (weight percent) of the major elements in cement (Ca, Al, Si, Fe, and S), the Si/Ca and S/Ca ratios using the rpart classification tree procedure (R package rpart; R Core Team 2022).

The rpart uses a two-step procedure to estimate a classification tree based on the material samples training data. First, a tree is built until no more reduction in misclassification can be achieved or until minimum leaf sizes are achieved. Second, the tree is pruned (simplified) based on cross-validation criteria. The cross-validation gives estimated misclassification errors with standard errors for the different pruned trees. As recommended in the rpart documentation, we used the one standard error rule to select the final classification tree. Any misclassification within one standard error is considered equivalent, and hence we selected the simplest model among those having estimated misclassification within this range. Default input parameters to rpart were used, except for the minimum number of observations in a node for which the routine will try to compute a split, which we set to 30. Technical details about the cross-validation procedure, split criteria and other aspects can be found in the r-part documentation (R Core Team 2022).

A significant fraction of beam electrons will leave the particles to the bottom or the side leading to a loss of X-ray intensity excited in the particles (characteristic radiation and Bremsstrahlung) as well as leading to a substantial contribution to the spectral background from the substrate (Small 2002). As both effects strongly depend on particle size, separate classification trees were constructed for particles with projected areas < 4 μm² and ≥ 4 μm².

Correction of proportions due to misclassification.

First, it was assumed that the true proportions were equal to those derived from the unadjusted classification. Then proportions were estimated with the classification matrix given in Table 1. The difference between these two proportions is the misclassification bias which was subtracted from the original proportions to obtain new bias-corrected estimates. This procedure for bias correction was tested on the material samples training set, and we found a clear reduction in bias for different proportions of clinker and limestone, see Supplementary material.

Classification of personal samples.

The personal samples were analysed by SEM-EDX as described above. We applied the classification tree determined for the material samples (training) data to classify particles by material type. Exposure to clinker was estimated by multiplying the AM of the SEM-EDX composition (expressed as weight proportion) with the AM thoracic aerosol exposure.

Determinants of the clinker content

Information on plant, job type and tasks that workers carried out during sampling was obtained from questionnaires completed on the same day as the sampling. Personnel from cement production plants working with production, cleaning, maintenance, laboratory, foreman, administrative personnel, and other job tasks were selected for the study. More details on job types have been published previously (Notø et al. 2015). Due to a small number of samples of some of the job types, workers were further grouped into three categories: (1) production (N = 16), (2) maintenance (N = 5), and (3) foremen (N = 4), laboratory (N = 1), cleaning (N = 2), and other (N = 6). Except for the two Norwegian plants, few measurements were performed in each plant. Plant was therefore treated as a random effect in the mixed regression model. Tasks were classified into three categories of increasing clinker content based on time spent on different tasks and assumed clinker content in the materials that were handled. This information had been collected *a priori* with a questionnaire completed by each worker at the end of the monitoring period. The two lowest categories were combined due to few observations in the lowest category (N = 3).

Data analysis

Data were described by arithmetic means (AM), and 10, 50, and 90 percentiles. Medians with 95% confidence intervals (95% CI) were estimated by quantile regression.

The effects of determinants on the clinker content of the thoracic fraction were estimated by linear mixed models. Proportions were logit-transformed to improve the normality of the data distributions. Components that were not detected in a sample were substituted by half divided by the total number of particles analysed in the sample. These data were analysed

Table 1. Classification of raw material particles, percentage of particles classified as the respective material type.

Material	Classified as, %								
	Limestone	Clay	Silica	Bauxite	Iron source	Coal fly ash	Coal	Gypsum	Clinker
Limestone	**71.7**	3.1	0.5	0.1	0.1	2.7	1.6	0.3	19.9
Clay	1.4	**66.6**	4.0	3.5	1.4	7.9	4.9	0.0	10.4
Quartz	0.3	11.7	**76.1**	0.4	2.7	3.8	2.9	0.3	1.9
Bauxite	1.0	10.3	0.0	**75.8**	4	1.9	3.1	0.2	3.7
Iron source	0.7	2.0	1.0	2.4	**87.5**	1.9	1.1	0.0	3.4
Coal fly ash	3.2	13.1	5.3	1.4	1.8	**64.5**	3.6	0.5	6.5
Coal	7.4	9.2	5.1	1.1	2.4	2.5	**64.1**	0.7	7.5
Gypsum	2.1	0.1	0.2	0	0.1	0.4	1.2	**80.5**	15.4
Clinker	10.0	0.3	0.2	0.2	0.1	0.1	0.9	3.0	**85.1**

using IBM SPSS Statistics, Version 25.0 (IBM Corp., Armonk, NY, USA) and R version 4.2.0 (R Core Team 2022).

Results

Few particles in the samples were aggregated which facilitated SEM-EDX analysis (Fig. 2).

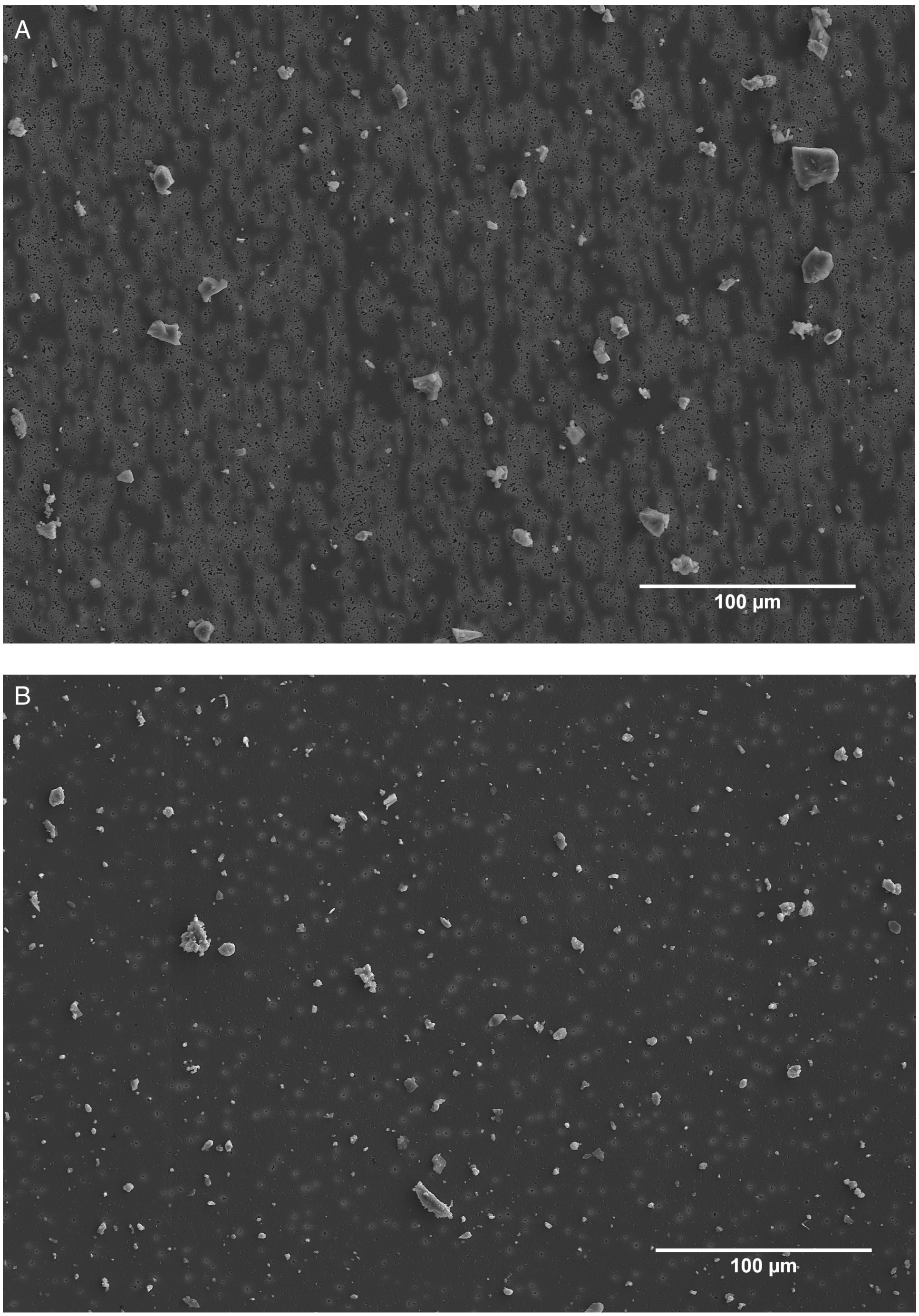

Fig. 2. SEM micrographs of personal samples of thoracic aerosols collected in the production department (backscattered electron imaging mode).

Particle classification

In total, 29 material samples were investigated: limestone (4), clay (5), bauxite (2), quartz (2), coal fly ash (2), iron source (2), clinker (6), gypsum (3), and coal (3). On average 938 particles were classified in each sample (total 27,217, range 407 to 1,942). For illustration, the simplest classification trees classifying all materials once are shown in Fig. 3.

To evaluate how well the classification performed on the training set, all particles in the training set were reclassified using the classification trees. Between 64% and 88% of the particles were classified as actual materials (Table 1). Clay, coal fly ash, and coal had the lowest percentage of particles classified as these materials (64% to 67%).

Particle size and shape of material and personal samples

Information on particle size and shape of the material and personal samples is given in Table 2 and Fig. 4.

For the different material samples, the particle size (equivalent projected area diameter) is rather similar (medians 1.01 to 1.35 µm, 10 percentiles: 0.60 to 0.66 µm; 90 percentiles: 2.31 to 3.33 µm). The particle shape is also quite uniform among material samples with the median aspect ratio varying between 1.42 and 1.53, except for coal fly ash which is more isometric with a median aspect ratio of 1.28 (Table 2). Particles from personal samples have a similar shape as the material samples (median aspect ratio: 1.48 versus 1.46, 10 percentiles: 1.22 versus 1.20 and 90 percentiles: 2.05 versus 2.01). The size distributions show considerable overlap (60%) but the particle size distribution of the personal samples extends to larger sizes (medians 1.65 versus 1.14% and 90% percentiles 4.88 µm versus 2.70 µm)

Composition of personal samples and exposure

The 53 samples that had been collected for the present study had an exposure level of AM 1.19 mg/m^3. Only 34 samples were suitable for SEM-EDX analysis and these had an AM of 0.73 mg/m^3. A total of 44,176 particles from 11 plants were analysed. On average 1,299 particles (range 300 to 9,306) were classified in each sample using the classification trees of the material samples. The proportions of all materials were computed for each sample. Fourteen proportions were not detected (4.6% of all proportions), 15% of bauxite, and 9% of clay, coal, and iron source.

The proportions of the different materials in the personal samples are shown in Table 3. The AM clinker content was 62.1% and the median was estimated to be 55.3% (95% CI 42.6% to 68.1%) of the thoracic mass and varied from 15.3% to 96.6% across samples. Limestone accounted for 14.8% (AM, median 13.2% and 95% CI 5.5% to 20.9%) whereas the other materials were present with relative abundances of median ≤ 6.4%. The proportion of silica was low (AM 1.9%, median 1.2, 95% CI 0.4 to 1.91, 0 to 1.7, median 1.3).

The exposure level of thoracic clinker was estimated to be AM 0.74 mg/m^3 by multiplying the AM clinker content with the AM thoracic aerosol exposure based on all collected samples (N = 53).

Determinants of the clinker content

Job type and task were explored by mixed model regression with the plant as a random effect, Table 4. Job type was not significant and showed relatively small differences between the categories, 66% to 80%. The clinker content in measurements when materials with high clinker content were handled was significantly higher than when materials with lower clinker content were handled, 85% versus 65% (P = 0.02).

Discussion

Methodological issues

Sampling and sample preparation.

The raw materials used for clinker production are likely to vary in composition and purity between the cement plants because they are obtained from different sources. Clinker as well as gypsum added to clinker to make cement are likely to be of higher purity than the raw materials. Still, some compositional variation can also be expected for these two components. Therefore, 2 to 6 samples of each material were included in our analysis to ensure that the potential variation is reflected. To improve comparability, material samples were obtained from factories that provided most of the personal samples (71%).

As particle size has a strong influence on the intensity of emitted X-rays, we attempted to collect particles from the material samples that were of similar size and shape as particles in the personal samples. The particle size in personal samples was slightly larger than in material samples (Table 2) with median particle diameters of 1.61 and 1.14 µm. Aspect ratios were almost identical with median ratios of 1.48 and 1.46, respectively. These slight differences are expected to have only a minor influence on the results of the classification procedure.

Particles must be sufficiently separated before analysis by SEM-EDS to avoid interference from adjacent particles as high particle densities on the substrate will lead to "artificial" mixtures, i.e. particles which had been separate particles in the airborne state may have been deposited at the same location on the filter

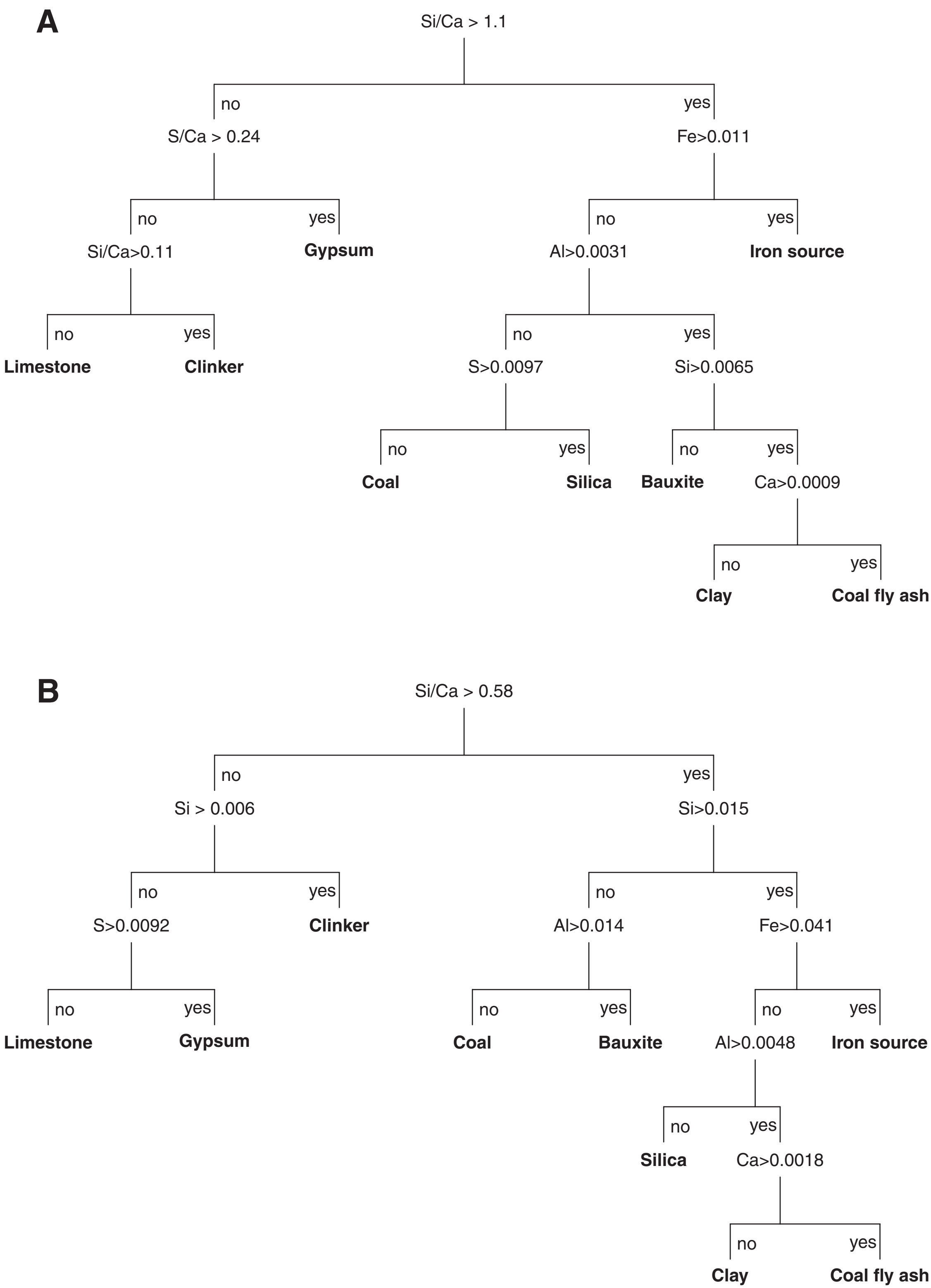

Fig. 3. Examples of classification trees for small particles with projected area < 4 μm² (A) and ≥ 4 μm² (B). Elemental mass fractions and element mass ratios are shown for the main elements in cement: calcium (Ca), silicon (Si), aluminium (Al), iron (Fe), and sulphur (S).

Table 2. Particle shape and size of material and personal samples.

Sample	K^a	N^b	Aspect ratio			Diameter[c], µm		
			10%	50%	90%	10%	50%	90%
Limestone	4	3,683	1.20	1.43	1.93	0.62	1.10	2.47
Clay	5	3,251	1.21	1.47	2.04	0.66	1.16	2.66
Quartz	2	1,997	1.24	1.53	2.14	0.60	1.13	2.69
Bauxite	2	1,927	1.19	1.42	1.92	0.61	1.24	3.22
Iron source	2	1,956	1.23	1.49	1.99	0.60	1.04	2.66
Coal fly ash	2	2,577	1.12	1.28	1.76	0.65	1.28	2.66
Coal	3	2,838	1.23	1.52	2.15	0.61	1.35	3.33
Gypsum	3	1,721	1.20	1.47	2.13	0.60	1.01	2.31
Clinker	6	7,267	1.22	1.46	2.00	0.60	1.09	2.54
All material samples	29	27,217	1.20	1.46	2.01	0.61	1.14	2.70
Personal samples	34	44,176	1.22	1.48	2.05	0.71	1.65	4.88

[a]Number of samples; [b]number of classified particles; [c]equivalent projected area diameter.

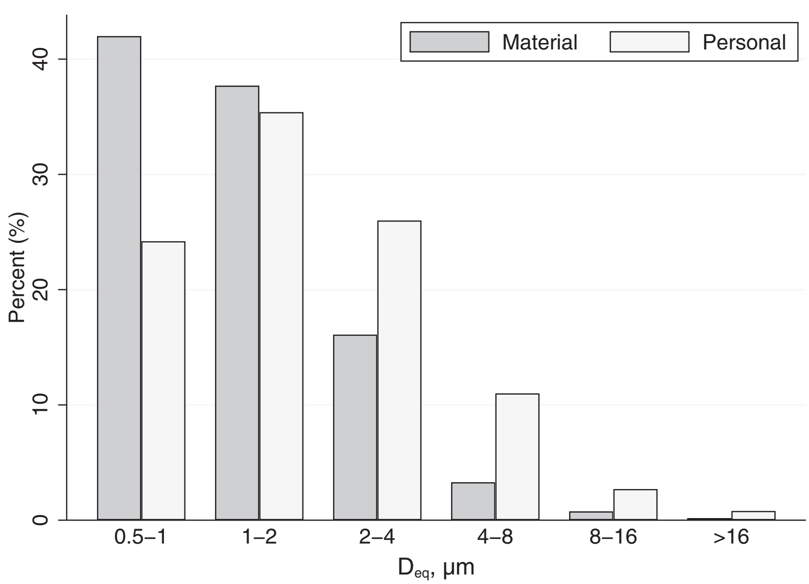

Fig. 4. Size distributions of particles in material and personal thoracic aerosol samples collected in cement production plants measured by SEM. Deq = equivalent projected diameter.

substrate. According to Kandler et al. (2018), the surface coverage of particles should not exceed a few percent. Aggregates were observed in the samples but their number was not regarded as a problem.

SEM-EDX analysis

The estimation of particle size, volume, and weight is subject to uncertainty. The almost identical aspect ratios of particles in material and personal samples indicate that particle shapes are comparable and which further indicates that the particles are reasonably isometric differences between individual material types were somewhat larger as their median ARs varied between 1.42 and 1.53, while coal fly ash that was more spherical (AR = 1.29). Most materials present in cement plants have similar densities provided that the particles are compact except coal which had a density approximately half of the other materials. The volume of coal particles was multiplied by 0.5 to adjust for this difference.

Table 3. Mineral weight proportions in personal thoracic samples of cement production workers (N = 34).

Material	Proportion, %					
		Percentiles				
	AM	10	50	90	Median[a]	95%CI[a]
Clinker	62.1	38.7	57.2	90.1	55.3	42.6–68.1
Limestone	14.8	0.1	13.2	31.3	13.2	5.5–20.9
Coal	4.0	0.1	2.0	7.6	2.0	0.0–4.0
Coal fly ash	11.8	2.5	6.7	23.8	6.4	4.7–8.1
Gypsum	4.2	0.8	3.0	8.5	3.0	2.2–3.7
Clay	1.1	0.0	0.1	3.8	0.1	0.0–0.2
Iron source	1.4	0.0	1.2	2.9	1.2	0.6–1.7
Silica	1.9	0.1	1.3	4.7	1.2	0.4–1.9
Bauxite	0.7	0.0	0.3	1.7	0.2	0.0–0.5

[a]Estimated by means of quantile regression.

Particle classification

The classification trees developed in the present study classified between 64% and 88% of the particles in material samples as the materials in the training set (Table 1). In principle, the development of classification trees is based on the assumption that the materials used in the training set are pure, i.e. only contain the material declared. However, X-ray diffraction analysis of bulk clinker samples from the plants studied (unpublished data) revealed that they contain several wt.% of non-clinker minerals (mostly carbonates and silicates). The presence of such impurities will contribute significantly to the observed misclassification. It is also likely that the other material samples in the present study are not pure. The extent of misclassification also depends on the complexity of the composition of the material samples. Misclassification was highest for clay, fly ash, and coal (33% to 36% misclassified), materials with a composition that may vary considerably. In contrast, materials with a more limited compositional variation (clinker, gypsum, and quartz) were classified more consistently (76% to 85%). A correction procedure was developed to correct for misclassification bias (Supplementary materials).

It is not known to what extent the failure to take into account heterogeneity in particle geometry may contribute to systematic errors in particle classification. However, as we collected particles of material and personal samples with similar size and aspect ratio distributions, it can be expected that the geometric effects are of similar magnitude, i.e. classification will not be affected much. In addition, one of the plants studied in the present paper was investigated earlier by Ervik et al. (2022) applying a different classification procedure. The authors collected a stationary sample at each of the three locations in the production department. These measurements showed that the aerosol composition was as expected from the type of processed material; limestone dominated at the raw meal mill, clinker at the clinker conveyer belt, and clinker and limestone at the cement mill. At the latter location also gypsum, an additive of Portland and blended cements, was detected. The personal samples in the present study represent an average of the exposure at the locations where operators had been working and cannot be compared directly with the Ervik et al.'s (2022) study. However, as both studies find that clinker is the major component and limestone is the second most abundant mineral, they are qualitatively in agreement.

For clinker and limestone, the two most abundant particle types in the personal samples, most of the misclassified particles belong to one group only (clinker erroneously classified as limestone, and limestone erroneously classified as clinker). Thus, the combined error for both groups will be substantially smaller in the personal samples than judged from the individual classification errors given in Table 1. For the other components, misclassification patterns are more complicated as more materials contribute to the combined misclassification errors. These positive errors compensate partly for the negative misclassification of a component. When we assume that the misclassification shown in Table 1 is correct, the clinker content in personal samples is underestimated by 2.3%, and limestone and silica are overestimated by 0.3% and 0.5%, respectively.

The data shown in Table 1 should not be regarded as a measure of accuracy, because the particles classified were also used as training sets. We, thus, prefer the term consistency of classification. Estimation of accuracy would require investigation of independent standard samples (i.e. samples with known particle abundances). Instead, the results of our classification procedure were roughly comparable to the previous findings of Ervik et al. (2022) which showed the same dominating materials (clinker and limestone) in the workplace aerosol. The latter group classified particles based on predefined chemical boundary conditions (Kandler et al. 2007; Anaf et al. 2012).

Personal samples

Clinker.

As clinker is expected to be the agent of most concern for respiratory health because of its highly alkaline and irritating properties, we focused further on this component. Clinker was the major material in the aerosol that cement production workers were exposed to, accounting for 55.3% of the aerosol mass estimated from the particle volumes. This estimate is fairly precise with

Table 4. Estimated clinker content in personal samples by job type and task using plant as random intercept in linear mixed models. Clinker content logit transformed prior to analysis. (Footnote *: Back transformed by inverse logit transformation.)

Determinant	N	Logit of proportion		P	Content (%)	
		Mean	95% CI		Mean*	95% CI*
Fixed effects						
Job type						
Production	16	0.85	0.26–1.43	REF	70	56-81
Maintenance	5	1.39	0.46–2.32	0.31	80	61-91
Foremen, cleaning, laboratory. and other	13	0.66	−0.03–1.35	0.61	66	49-79
Task						
Low/mixed clinker	27	0.63	0.10–1.16	REF	65	53–76
High clinker	7	1.72	0.92–2.52	0.02	85	71–93
Random effects		Variance				
Plant		0.209				
Error		0.794				
Total		1.003				

*Back transformed by inverse logit transformation.

a 95% CI of 49.1 to 61.3, was probably underestimated by 2.1%, and has external validity because it is based on measurements in 12 cement plants located in five different European countries and Turkey.

Hahn et al. (1998) estimated the Portland cement content in personal aerosol samples of inhalable dust during the handling of finished products in one cement production plant that ranged from 66% to 119% (N = 5, AM 86%; the highest value was ascribed to analytical uncertainty). As the clinker content of Portland cement is ≥ 95% (Comitè Europèen de Normalisation (CEN) 2011), the clinker content of the personal aerosol samples is then 82%, which is higher than found in the present study. There are several explanations for this difference: (1) The study by Hahn et al. (1998) may have overestimated the clinker content as was recognized by the authors; (2) the present study included production workers working at different locations, while Hahn et al. (1998) measured exposure during handling of cement. We found a clinker proportion of 66%, when high clinker tasks were carried out; (3) production of blended cement has increased in the 21st century. Such cements contain additives such as coal fly ash as well as limestone and contain less clinker than Portland cement. (4) It is further possible that the particle size fraction plays a role as larger particles contained more clinker than smaller particles near a clinker conveyer belt and close to a cement mill (Ervik et al. 2022).

Peters et al. (2009) found a proportion of 74% cement in inhalable dust exposure measurements in one cement production plant (AM, N = 6) based on the detection of Ca as a marker of cement. This proportion is overestimated because additives such as limestone and gypsum also contain calcium. We found that cement production workers were exposed to dust containing approximately 15% limestone and 4% gypsum (Table 3).

The estimates from the studies by Hahn et al. (1998) and Peters et al. (2009) are based on a small number of inhalable samples at a single plant in Germany and may have overestimated the clinker content. Therefore, our estimates of 55.3% in cement production workers in general and 66% among those working with high clinker materials seem to be more accurate for the thoracic particle size fraction.

Determinants of clinker content

Plant was treated as a random effect because we repeated samples per plant and the number of samples per plant was highly variable.

The small and not significant differences in clinker content between job types (66% to 80%) imply that cement production workers are on average exposed to aerosols with a similar clinker content. As the dust composition has been shown to vary between different locations in a cement plant (Ervik et al. 2022), the small differences in clinker content between job types are probably due to the high mobility of workers throughout the plant. It is interesting that the clinker content was significantly higher in tasks anticipated to have the highest clinker content than in lower clinker tasks (85% versus 65%; Table 4). This indicates that the classification method produces meaningful results.

Exposure

The mean exposure level of thoracic aerosol in the present study was (AM 1.19 mg/m^3). Only the samples with low particle density were analysed due to the requirements for SEM-EDX analysis, and these samples (AM 0.73 mg/m^3) underestimated the exposure level by 39%. Clinker exposure in the present study can be estimated to AM 0.74 mg/m^3 by multiplying the mean exposure aerosol level with the estimated clinker proportion assuming that the clinker content in the omitted samples is the same. This level applies to all job types because differences in clinker content between job types were not significant.

Limitations of the study

The main limitations of this study are the small sample size and the selection of samples with low particle density required for analysis by SEM-EDX. The number of material and personal samples that could be included in the study was constrained by the time required for analysis, and several personal samples could not be analysed because of a too high particle density on the sampling substrate. The results are therefore limited to samples from low-exposed areas or with short sampling time. The exposure estimation of clinker depends on the assumption that the clinker content in the unselected samples is similar to those that were analysed. The number of samples per plant was also unbalanced for feasibility reasons.

Conclusions

The composition of personal samples of mineral aerosols in the cement production industry could be estimated by automated single particle analysis with SEM-EDX and classification by a classification tree procedure.

Clinker was the major component in the thoracic aerosol that cement production workers are exposed to and amounted to 55.3% (95 CI 49.1 to 61.1) of the particle mass. Differences between job types were relatively small and not significant. However, the clinker content in samples when materials with high clinker content were handled was significantly higher than when materials with lower clinker content were handled, 85% versus 65% ($P = 0.02$).

Clinker exposure was estimated to be AM 0.74 mg/m^3 in this subset of the main study.

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Conflict of interest statement

The authors declare no conflict of interest relating to the material presented in this article. Its contents, including any opinions and/or conclusions expressed, are solely those of the authors.

Data availability

The datasets analysed during the current study are available from the corresponding author upon reasonable request.

Supplementary material

Supplementary material is available at *Annals of Work Exposures and Health* online.

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