APPENDIX C

Mortar-bar details and test results up to 12 months

Mortar-bar Set No:	1A	2A	3A	1B	2B	3B	4A	5A	6A	4B	5B	6B	4C	5C	6C	4D	5D	6D	7A	7B	8A	8B	9A	9B	9
Binder Proportions, %:																									
- Northfleet OPC	100	70	30	-	-	-	100	70	30	-	-	-	-	-	-	-	-	-	100	-	30	-	30	-	30
- Plymstock OPC	-	-	-	100	70	30	-	-	-	100	70	30	100	70	30	100	70	30	-	100	-	30	-	30	-
- A ggbfs	-	30	70	-	30	70	30	30	70	-	30	70	-	30	70	-	30	70	-	-	70	-	70	-	70
- B ggbfs	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	70	-	70	-
Alkali Content of Binder, % by wt:																									
- Acid soluble, Na_2O eq.	0.54	0.59	0.65	1.02	0.92	0.80	0.54	0.59	0.65	1.02	0.92	0.80	1.02	0.92	0.80	1.02	0.92	0.80	0.54	1.02	0.67	0.81	0.67	0.81	
- Water soluble, Na_2O eq.	0.12	0.09	0.05	0.55	0.39	0.18	0.12	0.09	0.05	0.55	0.39	0.18	0.55	0.39	0.18	0.55	0.39	0.18	0.12	0.55	0.08	0.21	0.08	0.21	
Aggregate Proportions, %:																									
- Flint coarse	60	60	60	60	60	60	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	60	-	-	
- Flint sand	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	60	60	40	40	40	60	
- Limestone coarse	-	-	-	-	-	-	60	60	60	60	60	60	60	60	60	60	60	60	40	40	60	-	60	40	
- Limestone fines	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Chloride Content, Cl^-, % by wt. of cement:																									
- As per Ingredients	0.03	0.05	0.12	0.03	0.05	0.12	0.02	0.02	0.07	0.02	0.02	0.07	0.02	0.02	0.07	0.02	0.02	0.07	0.02	0.02	0.15	0.15	0.10	0.10	
- After NaCl added	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.50	0.50	0.50	0.50	
Mean Expansion, % $x10^{-3}$																									
After, 14 days	6	4	9	9	14	12	1	-1	4	18	15	8	19	10	2	21	11	6	-6	13	2	1	17	20	
1 month	9	5	16	13	18	19	3	2	9	23	21	12	21	15	6	24	16	15	-5	16	5	3	15	19	
2 months	8	6	18	15	19	21	4	1	11	27	22	14	27	16	8	30	18	17	Nil	19	8	5	16	18	
3 months	8	6	17	18	18	21	3	1	9	29	23	13	28	16	6	30	18	15	Nil	22	6	5	18	21	
4 months	11	1	21	19	14	26	6	-3	8	31	19	12	29	19	7	34	19	17	-6	24	11	8	18	20	
5 months	7	2	18	14	17	21	3	1	6	34	24	11	32	16	6	39	21	15	-5	19	8	6	14	18	
6 months	7	2	18	14	18	20	3	1	6	31	25	10	34	18	7	37	19	16	-3	20	9	5	13	16	
7 months	8	-2	17	16	14	22	4	Nil	6	33	23	8	33	15	5	38	20	14	-3	22	5	Nil	15	18	
8 months	6	-1	14	15	13	19	2	-1	6	31	23	8	29	14	4	34	19	15	-4	21	10	3	15	15	
9 months	8	-1	17	13	15	21	1	1	5	32	26	8	33	18	3	37	21	12	-5	19	8	2	13	14	
10 months	4	-2	16	8	19	19	7	1	3	37	24	6	32	17	4	34	20	11	-7	14	12	4	13	15	
11 months	1	-4	12	8	14	18	2	-4	5	31	21	4	30	17	1	31	21	9	-7	15	9	3	13	16	
12 months	Nil	Nil	11	6	12	18	3	-6	4	29	18	4	33	12	4	35	14	12	-7	15	7	1	13	19	
Curve given in Figure:	1	1	1	2	2	2	3	3	3	4	4	4	5	5	5	6	6	6	7	7	8	8	9	9	9

POTASSIUM SULFATE IN KILN DUST

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1. ABSTRACT

An x-ray diffraction technique using the method of standard additions has been developed for the quantitative measurement of the potassium sulfate content of cement plant kiln dust. Numerous kiln dust samples have been analyzed via this method with very satisfactory results. The concentration of potassium sulfate varied strongly between samples, depending upon their respective origins. Large sodium concentrations were found to inhibit the potassium sulfate formation, and thus, limit the usefulness of this method. Results are also presented for the determination of potassium sulfate in size-fractionated kiln dust samples. The concentration of potassium sulfate was found to increase as the particle size decreases.

2. INTRODUCTION

Each year thousands of tons of kiln dust are produced by the cement industry. This dust contains a mixture of raw kiln feed, partially calcined material, finely divided cement clinker, and alkali salts (usually sulfates). Since the components of the kiln dust are much the same as the raw materials, some of the dust can be recycled into the kiln. However, even though over ninety-nine percent of the dust can be collected /1/, in some cases only about fifteen percent can be directly reintroduced into the kiln. This condition is due to the quantity of alkali sulfates in the dust and their adverse effects on the properties of the finished concrete product.

The major portion of the alkali sulfates found in the kiln dust are formed in the cement kiln hot zone. The alkalies, sodium and potassium, are generally present, although in small amounts, in both silicate clays and limestone. In the hot zone, where kiln temperatures reach 1500 deg. C., both sodium and potassium are fairly volatile. If a sulfur containing fuel is used to fire the kiln, SO_3 will be present in the combustion gases traveling toward the top of the kiln. Both sodium and potassium react readily at these temperatures to form sulfate. It has been shown /2/, that given equimolar quantities of Na_2O and K_2O in the presence of SO_3, three times as much K_2SO_4 will be formed as Na_2SO_4. Potassium sulfate formed in this manner exists as very small particles and nearly all of it is carried out the top of the kiln by the combustion gases.

While the reduction of potassium from the clinker materials is beneficial to the cement process, its presence in the kiln dust creates a by-product of limited value. If the potassium sulfate was removed, more of the dust could be reused. However, in general, cement manufacturers have had only minor success

in removing the alkalies from the dust. This is due to the fact that, while the simplest, most economical method of accomplishing this is by leaching the sulfates from the dust with water, in most cases water use and disposal problems are considerable. Recently, the general application of tight specifications on effluent water has practically eliminated interest in leaching.

With emphasis shifting toward conservation of natural resources, studies have been conducted regarding the marketability of kiln dust /3-5/. Strong efforts have been made to find markets for kiln dust, and though it has found a limited use as a fertilizer or soil supplement /3/, most attempts to sell the material have failed. More often than not, waste kiln dust is stored on site until it can be transported to and dumped into old quarries. This procedure can become very costly, especially if the dust must be shipped any great distance. In addition, water pollution may occur due to the unintentional leaching of alkalies into the ground water, by the percolation of rain through stored piles of kiln dust.

3. EXPERIMENTAL

3.1 Equipment

The x-ray diffraction patterns used for the qualitative analysis of the kiln dust samples were obtained on a Picker x-ray diffractometer. The patterns used for quantitative measurements were obtained with a Philips-Norelco unit. Both instruments used Ni filtered Cu K-alpha radiation and similar working conditions. The flame emission analyses were done with a Perkin-Elmer Model 4000, atomic absorption/flame emission spectrophotometer. Particle size fractions were obtained using ASTM standard mesh sieves for particles greater than 45 microns (mesh 325) and a Bahco microparticle classifier for smaller particles.

3.2 Materials

Twenty-seven kiln dust samples were obtained from portland cement plants in different sections of the country. X-ray powder diffraction patterns were taken for each sample, in order to qualitatively determine its composition. The composition of each sample was identified by comparing these patterns with data taken from the ASTM powder x-ray diffraction file.

An artificial kiln dust was prepared using quantitative data from Meade /6/, which closely approximates our own observations. All chemicals used were MCB reagent grade. To insure homogeneity the artificial kiln dusts were mixed in a Porcelain Jar, Ball Mill for 24 hours. Mixtures were prepared containing 5, 10, 15, 25, 50, 75, and 90 percent by weight K_2SO_4. A sample was also prepared containing no K_2SO_4.

3.3 Procedure

Specimens for qualitative identification by x-ray diffraction were mounted on aluminum sample holders measuring 3mm x 25mm x 50mm with a square depression on the flat side of one end. The depression was filled with dust, which was lightly pressed into place with a stainless steel spatula. No prior sample preparation was performed. The sample was aligned vertically in the x-ray beam and scanned over the range 20 to 60 degrees 2-theta. Corresponding d-spacings, determined from the patterns, were used for identification of the sample constituents. Patterns were repeated to assure that unrepresentative patterns were not being produced due to preferred orientation effects.

The potassium content of the kiln dusts was determined quantitatively with the use of flame emission spectrometry. The basic sample preparation procedure briefly described below, has been reported previously by Crow, Hime, and Connolly /7/ for use with portland cement.

One-half gram of cement kiln dust was placed into a beaker and dispersed with 25 mL water. Five mL of concentrated HCl were added and the solution was stirred to break up lumps. The sample was covered with a watch glass and digested on a steam bath for 15 min. at a temperature just below boiling. The resulting solution was filtered using a Buchner funnel and Whatman #1 filter paper. The filtrate was washed with hot 1% (v/v) HCl and several times with hot water. The solution was cooled to room temperature and diluted to 100 mL in a volumetric flask. This was then used as an initial working solution. Because of the large quantities of potassium in some of the dusts, dilutions of the working solution had to be made to keep the emission meter on scale.

The method of standard additions was used with x-ray powder diffraction to determine the concentration of potassium sulfate, in much the same way it is used to determine other species with atomic absorption spectroscopy /8/ and polarography /9/. The potassium sulfate peak at 29.75 deg. 2-theta (3.001 Angstrom d-spacing, 77% relative intensity) was used in this investigation since the 100% relative intensity peak at 30.77 deg. 2-theta (2.903 Angstrom d-spacing) could not be quantitatively measured due to the overlap of another K_2SO_4 peak at 30.96 deg. 2-theta (2.886 Angstrom d-spacing, 53% relative intensity).

An x-ray diffraction pattern was obtained for a sample containing an unknown percentage of potassium sulfate, and the intensity of the desired peak, I_1, was measured. A small amount, W_k, of reagent grade K_2SO_4 was then added to a given weight, W_u, of the unknown. An x-ray diffraction pattern was then run of this sample, and the intensity, I_2, was measured. The K_2SO_4 percentage in the unknown sample can then be calculated from the equation:

$$\% K_2SO_4 = f_u \times 100 = \frac{W_k \times I_1}{(W_k + W_u) \times I_2 - W_u \times I_1}$$

where f_u is the weight fraction of K_2SO_4 in the unknown sample.

4. RESULTS AND DISCUSSION

Table I lists the x-ray powder diffraction lines observed for a representative kiln dust sample, along with the d-spacing corresponding to each line. The data presented is consistent with and can be totally accounted for by $CaCO_3$, K_2SO_4, $CaSO_4$, CaO, SiO_2, and $(Na,K)_2SO_4$. All of these compounds were identified as being present to some degree in nearly every pattern run during this study. In all but a very few cases, it was obvious that $CaCO_3$ was the major component of the kiln dust. K_2SO_4 and $CaSO_4$ also appeared as significant components, while the other compounds tended to show up in minor quantities. In several of the dusts, other compounds, such as Na_2SO_4 and Al_2O_3, were identified, but always as a minor constituent.

The eight size-fractionated samples were taken from the kiln dust sample described in Table I and as such their diffraction patterns were all qualitatively identical with that shown. The intensities of the peaks associated with the K_2SO_4, however, successively increased from fraction 6 (-7.8microns) through fraction 8 (-2.4microns) with little or no K_2SO_4 identified in the patterns of larger particle size fractions. This indicates a direct dependence

of K_2SO_4 content on the kiln dust particle size. This dependence is shown in Figure I.

Table I. X-ray Diffraction Data for Kiln Dust

observed d-spacing	relative intensity	Identity (d-spacing)
4.26	5	SiO_2 (4.26)
4.16-4.18	5	K_2SO_4 (4.16, 4.176)
3.86	10	$CaCO_3$ (3.86)
3.49-3.51	17	K_2SO_4 (3.508), $CaSO_4$ (3.498)
3.34-3.39	35	SiO_2 (3.343), K_2SO_4 (3.384)
3.14	12	K_2SO_4 (3.14)
2.95-3.05	100	$CaCO_3$ (3.035), K_2SO_4 (3.001), $(Na,K)_2SO_4$ (2.95)
2.88-2.91	15	K_2SO_4 (2.903, 2.886)
2.84-2.85	14	$CaCO_3$ (2.845), $CaSO_4$ (2.849), $(Na,K)_2SO_4$ (2.84)
2.77-2.78	15	CaO (2.778)
2.49-2.52	15	$CaCO_3$ (2.495), K_2SO_4 (2.499, 2.518)
2.40-2.43	22	K_2SO_4 (2.386), CaO (2.405)
2.32-2.38	20	K_2SO_4 (2.374, 2.386), $CaSO_4$ (2.328)
2.285	18	$CaCO_3$ (2.285)
2.23-2.24	8	K_2SO_4 (2.23), SiO_2 (2.237)
2.20-2.21	6	K_2SO_4 (2.206)
2.08-2.10	25	$CaCO_3$ (2.095), K_2SO_4 (2.089, 2.082), $CaSO_4$ (2.086)
2.00-2.04	23	K_2SO_4 (2.002), $(Na,K)_2SO_4$ (2.04)
1.927	11	$CaCO_3$ (1.927)
1.913	20	$CaCO_3$ (1.913)
1.869-1.877	21	$CaCO_3$ (1.875), K_2SO_4 (1.87), $CaSO_4$ (1.869)
1.850-1.855	7	K_2SO_4 (1.855), $CaSO_4$ (1.852)
1.604	15	$CaCO_3$ (1.604)
1.587	5	$CaCO_3$ (1.587)

The reasons for the rather small amount of K_2SO_4 in the larger particle size fractions are two-fold. First, the larger particles are less likely to be present, since their formation depends directly upon the availability of the smaller particles. The smaller particles act as nuclei around which more K_2SO_4 deposits to form the larger particles. Second, since the K_2SO_4 is formed in the hot zone of the cement kiln, the particles must travel several hundred meters to the mouth of the kiln. The larger the particle, the less likely it

is for it to be able to traverse this distance while tons of raw mix are tumbling in the opposite direction. Also, the heavier a given particle is the less distance the hot gases will be able to carry it, and in general, the larger the particle, the heavier it will be. The small amount of K_2SO_4 found in these larger particle size fractions is probably due to naturally occurring K_2SO_4 in the cement raw mix.

FIGURE I. 2.886 Angstrom Peak Intensity vs. Particle Size

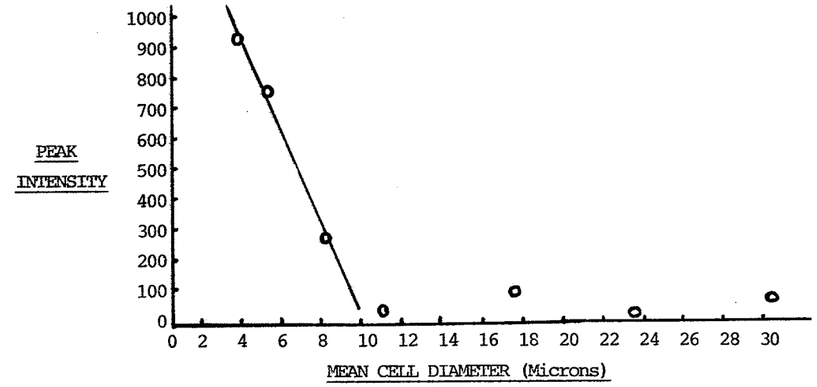

Table II presents data for the x-ray diffractometer calibration with known mixtures of artificial kiln dust and potassium sulfate. This data was fitted by linear least squares minimization to the equation: Peak Height = Slope x Weight Percent. A slope of 3.84 ± 0.11 was obtained. An attempt was made to analyze natural kiln dust samples in this manner, by simply dividing the K_2SO_4 peak height by the slope determined above. This method, however, was not successful, due primarily to variations between natural kiln dust matrices.

Table II. Calibration Data for the Quantitative Determination of K_2SO_4 in Artificial Kiln Dust

Weight % K_2SO_4	Peak Intensity (x 1/64 inch)
0.00	1.0 ± 6.4
4.96	17.8 ± 4.3
9.99	39.0 ± 10.2
15.01	57.0 ± 5.4
25.02	96.5 ± 20.3
49.99	193.3 ± 20.3
74.96	286.0 ± 18.7
89.98	346.4 ± 41.4
100.00	384.9 ± 39.4

The method of standard additions was used with x-ray powder diffraction to determine the K_2SO_4 content of the natural kiln dust samples. In addition, two artificial kiln dust samples, 5 and 25 percent by weight K_2SO_4, were run for control purposes. Table III shows the results of this study.[4] Data are presented for the percent potassium sulfate, as well as the percent sodium, determined by flame emission spectrometry. The K_2SO_4 figures determined by flame emission were calculated assuming that all the potassium in a given sample is present in this form. The large discrepancy between the flame emission and x-ray diffraction results for sample #KDN2 is probably due to the high sodium content of this dust, most likely in the form of $(Na,K)_2SO_4$. The sodium determination by flame emission spectrometry, as well as the presence of $(Na,K)_2SO_4$, obvious on the x-ray diffraction pattern, both support this argument.

Table III. Potassium Sulfate in Kiln Dust

	Theoretical	Experimental		
Sample #	% K_2SO_4	XRPD/% K_2SO_4	AE/% K_2SO_4	AE/% Sodium
KDN1	-------	3.48 ± 0.50	4.09 ± 0.03	0.01 ± 0.01
KDN2	-------	4.64 ± 0.48	27.50 ± 0.20	1.40 ± 0.03
KDA1	4.96	4.85 ± 0.99	5.05 ± 0.03	0.00 ± 0.00
KDA2	25.02	24.71 ± 1.48	24.78 ± 0.32	0.01 ± 0.01

Since the potassium in the kiln dust prevents it from being reintroduced into the kiln, it is the potassium content and not necessarily the potassium sulfate content which determines the reusability of the dust. The results of this study, however, indicate that while the determination of potassium sulfate does not account for all of the potassium in the kiln dust, in all but a few cases it is a good approximation. Since the mixed alkali salt, $(Na,K)_2SO_4$, was observed in these samples, it is probable that this salt accounts for the remainder of the potassium.

It is possible that the potassium in kiln dust can take other forms such as; (1) other potassium salts (KCl, KNO_3, etc.) and (2) potassium calcium silicates (as $KC_{23}S_{12}$). The relatively large amounts of sulfur oxides, available from burning coal, dilute the effects of other gases (as Cl_2, NO_2, etc.) which might otherwise combine with potassium to form other salts, making the contribution of potassium to kiln dust by these salts insignificant. Indeed, no other potassium salts were observed in any of the kiln dust samples.

The potassium calcium silicates are generally believed to form in the liquid phase of the clinker. If this is the case, it would be almost impossible for these compounds to reach the top of the kiln, and thus contribute potassium to the kiln dust. However, in order to search for such an unlikely contribution, $KC_{23}S_{12}$ was prepared in our laboratory. X-ray diffraction patterns obtained from this sample, as well as those from previous studies /10-12/, were compared with patterns obtained from the kiln dusts. There were no potassium calcium silicates observed in any of the kiln dust samples.

5. CONCLUSIONS

For the most part, the determination of K_2SO_4 using x-ray diffraction and the method of standard additions works quite well. Results agree fairly well with results obtained via flame emission spectrometry. The lower precision of the x-ray method is by far offset by the speed at which an analysis can be completed.

The reliability of this method obviously suffers when the sodium content rises and $(Na,K)_2SO_4$ is formed. It is, however, also obvious in these cases that $(Na,K)_2SO_4$ is present in fairly large quantities. There is no reason to believe that a similar method for the determination of this species will not also work.

The small amounts of K_2SO_4 found in particle size fractions greater than ten microns indicates that much of the kiln dust now being discarded could be reused if a suitable technique were developed to separate the smaller particles. A technique of this nature would save money and energy, and conserve our dwindling natural resources.

6. ACKNOWLEDGMENT

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