

## ANALYSIS OF CEMENT BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AND VOLUMETRIC METHOD

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**Summary**—A new method to determine the composition of cement raw mix and cement is devised. The sample was fused with a mixture of sodium carbonate and lithium tetraborate (3:1) at 925°C for 10 min. The fusion cake was dissolved in hydrochloric acid. The concentration of analyte in solution was either determined by atomic absorption spectrophotometry or titrimetry. The proposed method is quick and the analysis for interested oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{CaO}$ ) can be completed within 1 hr. The accuracy and precision are comparable to that of X-ray fluorescence spectrometry.

In cement manufacturing, raw materials such as limestone, shale, clay, iron and flyash are mixed in controlled proportions and ground to form a fine and homogeneous mixture called rawmeal (RM). The rawmeal is burnt at high temperature to give an intermediate product—clinker, which is interground with gypsum to form the construction product—cement. This process requires a large number of determinations, particularly for the elements Si, Al, Fe and Ca in a large number of different samples, *e.g.* rawmeal, clinker and cement. To have better control of quality, the method used must be rapid, accurate and with good precision.

The classical methods for cement analysis involve the gravimetric determination.<sup>1,2</sup> They are tedious and not suitable for on-line quality control purpose. The most popular method is X-ray fluorescence (XRF)<sup>3-6</sup> but the instrument is too expensive. Other instrumental methods applicable are UV-vis spectrophotometry,<sup>7,8</sup> atomic absorption spectrophotometry<sup>9,10</sup> (AAS), and inductive coupled plasma atomic emission spectrometry<sup>11</sup> (ICP).

In adopting the instrumental method such as AAS, the sample must be completely dissolved and fusion is generally used for converting the insoluble matrix to the acid soluble form. Fusion agents such as sodium carbonate, lithium tetraborate, lithium metaborate and sodium hydroxide have been reported for siliceous materials. The sodium carbonate cannot convert the silica completely to soluble form. The lithium tetraborate and lithium metaborate are most efficient for siliceous samples. Yet lithium metaborate is known to be

expensive and difficult to obtain with high purity. The lithium tetraborate although can have high purity, it takes a long time to digest the melt with acid. The sodium hydroxide requires the use of gold crucible. Thus for all the common fusion agents, each has its own disadvantage which means a new fusion system is needed that must be cheap, capable of dissolving the silica completely, and less time consuming.

In this paper, a new method is developed for rapid analysis of cement and rawmeal. Its objective is to provide an alternate method when X-ray fluorescence spectrometer is not available. This procedure involves a new fusion method where the fusion time required is shortened and the fusion cake is easily dissolved by acid. A classical method by means of titration and an instrumental method of using AAS are proposed to determine the oxides concentrations. The time required to analyse the four major oxides ( $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ) is within 1 hr. The precision and accuracy are better than the XRF.

### EXPERIMENTAL

Analytical reagent grade chemicals and distilled water were used throughout the procedure.

#### Instrumentation

A 'Hitachi' Z6100 Zeeman atomic absorption spectrophotometer was used for absorbance measurement. The conditions for elements interested were shown in Table 1.

Table 1. AAS instrument operating conditions

Element	Lamp current (mA)	Wavelength (nm)	Slit (nm)	Fuel type*	Flow rate	
					Fuel (l/min)	Oxidant (l/min)
Fe	7.5	248.3	0.2	A	1.5	15
Ca	7.5	422.7	0.2	A	1.7	13.6
Al	8.0	389.3	1.3	N	5.5	6
Si	8.0	251.6	0.4	N	5.8	6
Mg	7.5	285.2	1.3	A	1.7	15

\*A—air/acetylene flame; N—nitrous oxide/acetylene flame.

### Reagents

The fusing agent consisted of 1 g lithium tetraborate and 3 g sodium carbonate ground in mortar by a pestle to give a homogeneous mixture.

The lanthanum solution contained 30 g of lanthanum nitrate dissolved in 20 ml concentrated HCl, and then was diluted to 500 ml with distilled water.

The 15% m/v KF solution, 5% m/v KCl solution, and 5% m/v KCl ethanolic solutions, were prepared from a stock solution containing 5 g KCl dissolved in 100 ml 1:1 water ethanol mixture.

The preparation of phenolphthalein indicator required 0.1 g phenolphthalein dissolved in 10 ml ethanol. A 0.1M standard sodium hydroxide solution, 2% m/w KF solution, 20% m/w KOH solution, 50% v/v triethandamine solution, and 0.01M standard EDTA solution were all prepared.

The methylthymol blue indicator was prepared by adding 0.1 g methylthymol blue, finely ground, to 20 g potassium nitrate.

The sodium sulfosalicylate indicator contained 0.1 g sodium sulfosalicylate dissolved in 10 ml water with pH adjusted to 2.5.

An acetate buffer solution (pH 4.3) contained 42.3 g anhydrous sodium acetate dissolved in water; 80 ml glacial acetic acid was added and diluted to 1000 ml with distilled water.

The PAN indicator was prepared by dissolving 0.2 g of 1-(2-pyridylazo)-2-naphthol in 100 ml ethanol.

### Procedure

(A) *Atomic absorption spectrophotometry.* A 0.200 g sample was weighed accurately and mixed thoroughly with 0.8 g of fusion agent inside a platinum crucible. The crucible was covered by its lid and placed in muffle furnace at 925°C for 10 min. The crucible lid was then transferred to a 400 ml beaker containing 100 ml of boiling distilled water. The crucible was

cooled by washing its exterior wall with a stream of water. It was then placed in the same beaker. Twenty millilitres of conc. HCl was added and covered by a watch glass. The solution was heated until the fusion cake was dissolved. It was diluted to 500 ml in a volumetric flask. This sample solution was reserved for SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> determination. For CaO and MgO determination, 10 ml of sample solution used in silica determination was pipetted into a 100 ml volumetric flask and 4 ml of lanthanum solution was added and diluted to the mark with distilled water.

For standards preparation, 0.5000 g of cement standard, e.g. BCS 372/1 was mixed with 2.0 g fusing agent and treated similarly as for the sample. The sample solution was diluted to 250 ml in a volumetric flask and labelled as standard stock Solution A. Samples of 30, 40, 50, 80 ml of standard stock Solution A were pipetted separately to a series of 250 ml volumetric flasks and were diluted to mark with distilled water. These standard solutions were used for SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> determinations. The concentrations of these oxides in each standard solution were calculated by the following equation:

$$C_1 = C_0 \times V_0/50$$

$C_1$  = concentration in standard solution (%);  
 $C_0$  = standard known concentration (%);  
 $V_0$  = volume of standard stock Solution A pipetted (ml).

Standards for CaO and MgO determination were prepared by first fusing 0.2000 g of cement standard with 0.8 g fusing agent for 10 min. After dissolving by hydrochloric acid as in sample solution preparation, it was diluted to 500 ml in a volumetric flask and labelled as standard stock Solution B; 10, 20, 25 and 40 ml of this Solution B were pipetted separately into a series of 250 ml volumetric flask. Ten millilitres of lanthanum nitrate solution was added to each flask and diluted to mark with distilled

water. The concentration of each oxide in the standard solution is calculated by the equation below.

$$C_1 = C_0 \times V_0/25$$

$C_1$  = concentration in standard solution (%);  
 $C_0$  = standard known concentration (%);  
 $V_0$  = volume of standard stock Solution B used (ml).

The reagent blank solutions were prepared similarly as the sample solutions except that no sample was used in the fusion procedure.

(B) *Volumetric method.* A 0.5–1.0 g sample was accurately weighed into a platinum crucible and 3 g of fusion agent was added and mixed well. It was fused and dissolved as mentioned in Section A. The solution was transferred to a 250 ml volumetric flask and the beaker was washed. The washings were also poured into the flask. It was then diluted to mark.

For silica determination, 25 ml of sample solution was pipetted into a 600 ml plastic beaker and 10 ml of conc. nitric acid was added. Later 10 ml of 15% KF solution was added. Potassium chloride solid was added with stirring by a plastic rod to saturate the solution. The beaker was cooled to room temperature for at least 10 min. The content was filtered. The beaker and filter paper were washed several times with 5% KCl solution. The filter paper was put in the plastic beaker and 10 ml of 5% KCl ethanolic solution and 10 drops of 1% phenolphthalein were added. The content was then neutralized by 0.1M NaOH standard solution; 200 ml of boiling water was added and titrated with 0.1M standard sodium hydroxide solution. The % SiO<sub>2</sub> was calculated as

$$\% \text{SiO}_2 = \frac{15.02 \times M \times V}{W}$$

$M$  = molarity of NaOH;  $V$  = volume of titrant (ml);  $W$  = mass of sample (g).

In CaO determination, 10 ml of sample solution was pipetted into a 600 ml beaker and 2.5 ml of 2% KF solution was added. It was stirred and diluted to 200 ml with distilled water; 5 ml of 50% triethanolamine solution and 0.2 g methyl thymolblue indicator were added; then 6 ml of 20% KOH solution was added to adjust the pH to about 12. The solution was titrated by 0.01M standard EDTA solution until the blue color disappeared

$$\% \text{CaO} = 56.08 \times M \times V \times 2.5/W$$

where  $M$  = molarity of EDTA solution;  $V$  = volume of titrant.

To determine the iron oxide, 25 ml of sample solution was pipetted into a 600 ml beaker. One hundred millilitres of boiling water was added followed by 5–6 ml of 5% ammonium hydroxide to adjust the pH at around 1.8. Ten drops of sodium sulfosalicylate indicator were added. The solution was titrated by 0.01M standard EDTA solution to the end point of pale yellow. The iron oxide content was calculated as

$$\% \text{Fe}_2\text{O}_3 = 79.845 \times M \times V/W.$$

To the beaker where the iron determination had been done, 25 ml of 0.01M standard EDTA was added. It was diluted to 200 ml with boiling water and 15 ml of acetate buffer was added. The solution was boiled for 1 min and 6–7 drops of PAN indicator was added. The solution was immediately titrated with 0.01M standard copper(II) sulphate solution until it became purple.

$$\% \text{Al}_2\text{O}_3 = 50.98 \times M \times (25 - K \times V)/W$$

$K$  = molarity of CuSO<sub>4</sub>/molarity of EDTA.

## RESULTS AND DISCUSSION

To digest the siliceous samples, methods suggested include microwave digestion,<sup>12,13</sup> and fusion. The time required for microwave digestion is more than 1 hr which is not suitable. The fusion systems published are sodium carbonate,<sup>14</sup> lithium tetraborate,<sup>15,16</sup> lithium carbonate–boric acid,<sup>11</sup> and lithium metaborate.<sup>9,15</sup> The lithium tetraborate and lithium metaborate are effective to convert silica to soluble form but they have drawbacks in that they are more expensive and metaborate is difficult to purify. The boric acid system requires a longer fusion time of about 1 hr which is not suitable for routine work. With preliminary studies on sodium carbonate and lithium tetraborate, the sodium carbonate was found to attack silica less readily than the tetraborate but the time for the fusion cake to dissolve was much less than the borate system. Thus a system that was made up of different proportions of sodium carbonate and lithium tetraborate was studied. The advantages of reduced pretreatment time and comparatively cheaper are foreseen in this design. It was found that mixing three parts of sodium carbonate with one part of lithium tetraborate was the best system in

Table 2. Efficiency of different fusion systems

Sample type*	Known	Concentration (%) Found			
		Sodium carbonate	Lithium tetraborate	Proposed	
SiO <sub>2</sub>	Rawmeal	14.00	13.76	14.14	13.86
	Flyash	47.3	37.70	43.27	47.80
Al <sub>2</sub> O <sub>3</sub>	Flyash	29.8	31.34	30.52	30.83
Fe <sub>2</sub> O <sub>3</sub>	Flyash	12.8	12.07	11.26	11.96
CaO	Rawmeal	44.18	44.52	44.94	44.11

\*The flyash used was standard ASCRM 010. The known values in rawmeal were determined by XRF.

terms of efficiency and work time required. To compare the efficiency of the proposed system with others, samples were fused with different systems and analysed by AAS. The results are shown in Table 2.

There is no significant difference among the three systems in the recovery of iron, aluminium and calcium but the sodium carbonate is found to be inferior in silica determination. In fact, precipitate was observed during the dissolving of the fusion cake. Thus sodium carbonate alone is not recommended as the flux in the present work. On the other hand, the proposed system is better than the lithium tetraborate in terms of cost and working time required. In further optimizing the conditions, to prevent the effect of sputtering during fusion, covering with a lid can also improve the recovery. It was found that with lid, the recovery of CaO was improved from 98 to 100%. For the ratio of sample to fusion agent, there was no significant difference for the studied ratio ranging from 1:3 to 1:8.

In selecting the methods for determining the analyte in sample solution, the AAS method was chosen as the instrumental method because

its speed is faster than the visible spectrophotometry, common and cheaper than other instruments such as ICP. Among the classical method proposed, the gravimetric method used in SiO<sub>2</sub> determination is the main cause to slow down the speed of analysis. Therefore the volumetric method,<sup>17</sup> as mentioned in the National Standard of People's Republic of China was adopted as a testing method.

To test the recoveries of the method, special reference standards with high concentration of the oxide interested (*e.g.* A.R. CaCO<sub>3</sub> for CaO) were fused and analysed by both methods. As from Table 3 the recoveries for the five major oxides interested are all close to 100%. This indicates that the fusion system is effective to convert the insoluble oxide to acid soluble form. But in the volumetric method for iron and aluminium determination, the recoveries are greater than 100% where AAS method is more preferable. The possible explanation is that the titration of iron and aluminium at acidic medium may be positively interfered by the titanium because the titanium can also complex with EDTA at acidic medium. It was further verified by preparing a sample with an excep-

Table 3. Recovery of major oxides from reference standards using volumetric and AAS method

Sample type	Known concentration (%)	% Recovery		
		Volumetric method	AAS method	
CaO	CaCO <sub>3</sub> , A.R.	56.03	99.88	100.43
	Limestone BCS 393	55.4	99.97	99.87
SiO <sub>2</sub>	Flyash ASCRM 010	47.3	101.14	99.75
	Cement BCS 372/1	20.3	99.70	99.21
	Feldspar BCS 375	67.1	100.75	100.45
Al <sub>2</sub> O <sub>3</sub>	Flyash ASCRM 010	29.8	100.54	101.88
	Cement BCS 372/1	5.37	101.30	99.44
	Bauxite BCS 394	88.8	103.10	100.72
Fe <sub>2</sub> O <sub>3</sub>	Flyash ASCRM 010	12.8	102.97	93.13
	Cement BCS 372/1	3.42	104.67	100.58
	Flyash SRM 2690	5.10		96.47
	Iron ore BCS 676-1	56.85	98.82	98.5
MgO	Flyash SRM 2690	2.54		97.64
	Cement BCS 372/1	1.31		99.23

Table 4. Accuracy analysis

(A) Volumetric method	Concentration (%)			(B) AAS method	Concentration (%)			(C) XRF method	Concentration (%)			
	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO		Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO
Known Found Known Found Known Found	13.98	44.89	2.47	3.00	11.00	43.41	3.00	6.84	18.65	41.37	2.56	3.70
	14.06	44.32	2.62	3.06	11.07	43.35	3.16	6.83	19.02	41.42	2.47	3.81
	12.34	46.38	2.70	2.89	13.28	43.41	4.62	4.30				
	12.42	46.38	2.86	2.94	13.00	43.24	4.52	4.20				
	13.35	43.82	1.40	3.02	12.32	47.21	1.80	2.06				
	13.27	43.44	1.42	3.08	12.20	47.11	1.79	1.80				
Rawmeal												
BCS 372/1 Known Found	20.3	65.3	3.42	5.37	21.24	62.14	4.40	3.68	20.50	64.80	4.82	3.77
	20.24	64.89	3.58	5.44	21.31	62.14	4.30	3.66	20.62	64.90	4.63	4.26
BCS 353 Known Found	20.5	64.8	4.82	3.77	20.50	64.80	4.82	3.77	20.30	65.30	3.42	5.37
	20.55	64.77	4.79	4.01	20.54	64.09	4.60	3.84	20.80	64.18	3.53	5.76
BCS 354 Known Found	21.8	70.00	0.30	4.85	20.3	65.30	3.42	5.37				
	21.91	69.62	0.42	4.88	20.14	65.64	3.44	5.34				
Average difference	0.03 (0.08)†	-0.28 (0.19)	0.10 (0.08)	0.08 (0.08)	-0.06 (0.14)	-0.11 (0.34)	-0.04 (0.13)	-0.04 (0.08)	-0.40 (0.24)	0.32 (0.69)	0.11 (0.07)	-0.31 (0.19)
Cement												
BCS 1885 Known Found	20.3	65.3	3.42	5.37	21.24	62.14	4.40	3.68	20.50	64.80	4.82	3.77
	20.24	64.89	3.58	5.44	21.31	62.14	4.30	3.66	20.62	64.90	4.63	4.26
BCS 372/1 Known Found	20.5	64.8	4.82	3.77	20.50	64.80	4.82	3.77	20.30	65.30	3.42	5.37
	20.55	64.77	4.79	4.01	20.54	64.09	4.60	3.84	20.80	64.18	3.53	5.76

\*Raw mix standards were prepared by mixing different proportions of following reference standards: limestone BCS 393, silica BCS 313/1, Flyash ASCRM-101, SRM 2691, bauxite SRM 698, iron ore BCS 676-1, feldspar BCS 375 and 376.

†Values in parentheses are the standard deviation of the difference.

Table 5. Real samples analysis

	Concentration found, %														
	SiO <sub>2</sub>			CaO			Fe <sub>2</sub> O <sub>3</sub>			Al <sub>2</sub> O <sub>3</sub>			MgO		
	Proposed Tit.	AAS	XRF	Proposed Tit.	AAS	XRF	Proposed Tit.	AAS	XRF	Proposed Tit.	AAS	XRF	Proposed AAS	XRF	BS
Rawmeal	14.00	14.03	14.04	44.44	44.08	44.26	2.27	2.08	2.21	3.26	3.11	3.28			
	14.67 (0.08)*	14.60 (0.40)	14.58 (0.16)	43.81 (0.10)	44.11 (0.15)	44.18 (0.40)	2.36 (0.05)	2.24 (0.13)	2.29 (0.02)	3.14 (0.06)	2.93 (0.09)	3.10 (0.10)			
Clinker	16.53	16.32	16.52	42.07	43.70	42.71	2.41	2.32	2.20	4.69	4.54	4.94			
	9.41	9.35	9.38	47.52	47.40	47.10	1.25	1.21	1.27	2.80	2.48	3.08			
	21.70	21.04	21.56	68.21	68.31	67.37	3.05	3.05	2.80	5.69	5.44	5.43			
	21.49	21.91	21.60	66.22	65.76	65.73	3.22	3.23	3.26	5.73	5.66	5.50	1.03	0.94	
Cement	20.20	19.65	20.33	67.54	67.92	66.65	3.25	2.71	2.87	6.67	6.77	6.54			
	20.45	21.00	20.85	64.85	64.23	64.63	2.79	2.81	2.82	5.31	5.09	5.02	1.09	1.04	
	20.52	21.38	21.39	64.00	64.18	64.63	3.09	2.98	2.99	4.69	4.48	4.55	1.58	1.62	
	21.04	20.97	21.49	64.78	64.86	64.45	2.92	2.86	2.96	5.38	4.85	4.72	1.05	1.05	
Blended cement	(0.12)	(0.22)	(0.12)	(0.08)	(0.18)	(0.43)	(0.05)	(0.14)	(0.06)	(0.05)	(0.15)	(0.11)	(0.04)		
	21.14	21.20	21.34	65.01	65.12	65.12	2.97	2.81	2.88	5.60	5.49	5.40	0.53	0.70	0.80
	21.96	21.71	22.25	64.25	64.39	64.49	5.19	5.21	5.28	3.78	3.20	3.25	0.82		
													2.58	2.58	2.67
Flyash													(0.04)	(0.13)	(0.31)
													2.50	2.58	2.49
													(0.02)	(0.19)	(0.05)
												1.41	1.40	1.40	
												1.04	1.04	1.05	

\*Value in parentheses is the standard deviation of triplicate determination.

tionally high concentration of titanium. As the ratio of interferent to analyte was around 1–2, the recovery for titration method was about 116 and 167% for  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , respectively but the AAS method was unaffected by such a high concentration of titanium. Thus the volumetric method for iron and aluminium can only be accepted if  $\text{TiO}_2$  is only of negligible amount and it is the case as found in cement samples. On the other hand, high purity silica standard had been tried to test the  $\text{SiO}_2$  recovery but it was only about 70–80%. The problem was solved by adding calcium carbonate<sup>20</sup> which simulated the composition of cement rawmeal. Therefore in an accuracy test, the cement raw mix samples were specially prepared with certain amount of high purity silica to check if the conversion could be completed by the presence of calcium carbonate.

Accuracy of the method was checked by using standards with a more complex matrix. Cement reference standards and rawmeal standards prepared by mixing known proportions of reference raw materials (*e.g.* limestone, flyash, bauxite, feldspar, silica and iron ore) were employed. Results are summarized in Table 4. It shows that the fusion system can effectively convert different geological samples, *e.g.* limestone and flyash to soluble form. The accuracy is good and even better than the XRF method especially when the concentration of the analyte is out of the normal range. For the volumetric method, with the  $\text{TiO}_2$  at a level of less than 0.5%, its effect on iron and aluminium can be neglected and the method can be applied without special precaution.

In real sample analysis, cement rawmeal, clinker, cement, pulverized fuel ash and flyash blended cement were analysed by methods including XRF, fusion followed by AAS and titrimetry. From Table 5, there is no significant difference between the AAS and XRF method. But the volumetric method shows a systematic difference with XRF in the iron and aluminium determination. Therefore the volumetric method should be applied as the  $\text{TiO}_2$  is known to be at low level, *e.g.* <0.5% where the deviation is still within the tolerance level. On the other hand, as specified by the BS specifications,<sup>18,19</sup> for the flyash and blended cement, the MgO must be less than 4%. The standard/reference method suggested is too tedious and not suitable for routine work. When the proposed method is applied to these samples, the results obtained are in good agree-

ment with the BS method. This shows that the fusion followed by AAS can save a lot of time in determining the MgO in flyash or cement sample and suitable to replace the BS method in quality control of product manufacturing with accuracy comparable to reference method.

In the precision studies, triplicate determinations were carried out for the sample. The results are also listed in Table 5. The volumetric method gives the best precision and the AAS method is inferior to others but can still be accepted for on-line control as in cement production. In the MgO determination, the precision of the proposed method is much better than the XRF and BS method where the lengthy steps of extracting the magnesium from sample reduces the precision of the method. The poor flux yield of light element such as Mg and Na, in XRF analysis gives rise to the poor precision detected.

## CONCLUSION

A new fusion system is proposed for cement and cement rawmeal analysis. Two finishing methods are developed. These methods offer the advantages of time saving and expensive instrumentation such as ICP or XRF are not required. This is particularly important to those factories where XRF is not available. It also serves as a backup method for the XRF and as a cross check to the XRF analysis.

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