

Estimation of OPC, Fly Ash and Slag Contents in Blended and Composite Cements by Selective Dissolution Method

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Abstract—This paper presents the results of the study on the estimation of fly ash, slag and cement contents in blended and composite cements by selective dissolution method. Types of cement samples investigated include Ordinary Portland Cement (OPC) with fly ash as performance improver, OPC with slag as performance improver, Portland Pozzolana Cement (PPC), Portland Slag Cement (PSC) and composite cement conforming to respective Indian Standards. Slag and OPC contents in PSC were estimated by selectively dissolving OPC in stage 1 and selectively dissolving slag in stage 2. In the case of composite cement sample, the percentage of cement, slag and fly ash were estimated systematically by selective dissolution of cement, slag and fly ash in three stages. In the first stage, cement is dissolved and separated by leaving the residue of slag and fly ash, designated as R1. The second stage involves gravimetric estimation of fractions of OPC, residue and selective dissolution of fly ash and slag contents. Fly ash content, R2 was estimated through gravimetric analysis. Thereafter, the difference between the R1 and R2 is considered as slag content. The obtained results of cement, fly ash and slag using selective dissolution method showed 10% of standard deviation with the corresponding percentage of respective constituents. The results suggest that this selective dissolution method can be successfully used for estimation of OPC and Supplementary Cementitious material (SCM) contents in different types of cements.

Keywords—Selective dissolution method, fly ash, Ground Granulated blast furnace slag, EDTA.

I. INTRODUCTION

NOWADAY'S cement manufacturers produce different types of cements by using one or more than one mineral addition [1]. In view of this, different types of blended cements such as PPC, PSC and composite cements are available [2]. These blended cements play significant role to mitigate CO₂ emissions, clinker factor reduction sustainability, energy reduction and economic benefits [3]. Blended cements are cements in which part of the clinker is substituted with other materials. Of particular significance throughout the world are granulated slag from the production of pig iron, Fly Ash (FA) and unclaimed limestone. In line of this connection, governing bodies also encourage the development of blended cements by formulating the respective standards by defining the allowable percentage range of mineral admixtures in the respective blended cements. In view of the monitoring and controlling of the mineral admixture constituent percentage present in the respective blended cements, governing bodies

revised the adopted respective formulated codes by regulate to mention percentage of mineral admixture on the bag along with the other parameters from the manufacturer end [3]. As well as periodic quality check was carried out by the governing bodies to verify the declared percentage of mineral admixture by collecting the different samples from the market [3].

Cement plants were practicing the quality control parameters of produced blended cements by monitoring the chemical parameters of CaO, SiO₂, Al₂O₃ and other chemical parameters. Alternative methodology for validating the produced cement for PPC was insoluble residue method [5]. But this method shows inaccuracy of the results by correlating the calculated IR with the FA constituent percentage in the case if the FA itself do not have more than 85% of insoluble residue [6]. Moreover, as per the Bureau of Indian Standards no alternative methodologies are available for estimation of slag [4]. Several reports are published for quantitative estimation of FA and slag in PPC, PSC and composite cements using XRD using internal standard, external standard and partial or not known crystal structure analysis [7]-[9]. All these technologies require special expertise to obtain better results [10]. While the internal standard method has a problem with the achievement of homogeneity of the standard material with the cement, the external standard method suffers from X-ray absorption differences between the standard material and cement leading to quantification errors [10]. A recent idea to directly quantify the amorphous phase fraction in blended cements is the Partially or No Known Crystalline structures (PONKCs) or pseudo-phase characterization [7]. This technique records information about the mass, volume, and atomic number (ZMV) values of the commonly seen FA/slag amorphous phase and stores them into a pseudo crystal structure, called a PONKCs phase. The PONKCs amorphous phase can be refined similar to a crystalline phase to obtain the amorphous weight fraction. However, there lies a caveat in the PONKCs method with the creation of a proper amorphous pseudo-phase. The compositions of the FA produced in India vary considerably, and it is difficult to classify the FA or slags based on their mineralogical contents. Hence, the application of a single pseudo-phase for an amorphous FA or slag cannot be generalized over all FA or slags obtained from different sources [10]. Thus, a standard method is required for estimation of mineral admixtures in PPC, PSC and composite cements. This research paper overcame the short comes of the estimation of FA and slag in PPC, PSC and CC by selective

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dissolution method.

II. MATERIALS AND METHODS

Samples of clinker, gypsum, FA and slag were collected from the cement industries.

Two OPC samples were prepared with different quality of clinker by keeping the gypsum quality constant for 100 kg each in laboratory ball mill for 300 m²/kg fineness. Similarly, FA and slag were ground to 300 m²/kg fineness in laboratory ball mill of about 50 kg each. Known percentages of OPC with Performance Improver (PI), PPC, PSC and Composite Cement (CC) according to the Bureau of Indian standard [4], [5] allowed percentage were prepared by using inter mixing on the pot mill for about 1 kg of each sample. Ten samples of OPC with inter mixing of 1-5% of FA, Ground Granulated Blast Furnace Slag (GGBFS) separately, 10 samples of PPC with 15-35% of FA and 10 samples of PSC with 20 to 65% of GGBFS slag and 10 samples of CC samples with 15-35% of FA and 20 to 50% of slag samples were prepared in laboratory mill. Four market samples were also collected of PPC (one), PSC (one) and CC (two). All the cement samples were prepared for 8 kg quantity in laboratory ball for 300 m²/kg fineness with the stoichiometric percentage of mineral admixture/s. Chemical analysis of all the samples were carried out by relevant standards methods for ensure the homogeneity and representative ness of the sample.

Stock solutions of 0.05M EDTA, 1:1 ratio of Triethanol Amine (TEA), 5% H₃PO₄ and 0.1M NaOH solutions were prepared for 1 liter from the di sodium EDTA salt.

III. RESULTS AND DISCUSSION

It is difficult to estimate the percentage of OPC, FA and slag in composite cements by instrumental techniques such as XRD or FT-IR or SEM or TG-DTA. Because, if we consider example of XRD patterns of composite cements, the diffraction patterns of FA and GGBFS slag showed amorphous hump and overlap of peaks. Separation of these diffracted peaks and quantification of diffraction in the presence of amorphous by Reitveld method provides semi quantitative percentages of constituents [10]. Hence, physical separation of the mineral and their gravimetric estimation of individual portions like selective dissolution method for silicate mineral and aluminate minerals in clinker samples will be for quantification of minerals in blended cements [11]. Selective dissolutions offer the possibility of individually estimation of different minerals. In addition, for better identification, obtained residues from the respective minerals can be validated by other instrumental techniques such as XRD and FT-IR.

The selective dissolution methodology was formulated with three types of solutions for systematically dissolution of cement and slag.

EDTA with TEA: This solution or extraction dissolves calcium silicates and gypsum minerals and produces the residue of GGBFS slag and FA minerals [12]-[15]. Sodium containing EDTA-TEA solution acts as a good solvent for

dissolution of clinker and gypsum minerals. Sodium-based alkaline aqueous solution of ethylenediamine tetraacetate (EDTA) supplemented by the presence of 6% TEA acts as chelating system and dissolves clinker and gypsum minerals and shows a selective decelerating effect in the presence of TEA to release of minerals from the glassy compositions. Thus, it allows good separation and quantitative dissolution of OPC and BFS from the slag or CC. 125 ml of EDTA, 125 mL distilled water and 15 mL of 1:1 TEA with the adjustment of pH 11.6 ± 0.1 .

Solution 2-EDTA without TEA: Sodium-based alkaline aqueous solution of EDTA acts as chelating system and dissolves clinker, gypsum and slag minerals. Thus, it allows good separation and quantitative dissolution of OPC, GGBFS slag and gypsum from the CC. FA is obtained as residue after treatment with the second step. In this step, slag is extracted from the obtained residue of step 1 and produces FA as a residue. For this step, the EDTA solution of 125 ml was diluted to 250 ml by adding 125 ml of distilled water in a beaker and then the pH of the this solution was adjusted to 11.5 ± 0.1 by adding NaOH dropwise [4], [12]-[15].

Solution 3-H₃PO₄: Another methodology was also adopted to validate the above obtained results, i.e., treatment of residue 1 from the step 1 with 5% of H₃PO₄ solution. This H₃PO₄ solution dissolves slag minerals from the FA and slag compositions and produces FA as a residue. 30 mL of 5% H₃PO₄ and 30 mL distilled water solution were used for selective dissolution of slag. This step also allows good separation of slag and FA from the CCs [16].

Selective dissolution of cement, FA and GGBFS slag studies was conducted systematically on different qualities of OPC, FA and GGBFS slag with the above solutions at constant stirring time 30 mins and it is observed that cement dissolved 95-98% with the solution one and slag & FA is obtained as a 100% residue with the solution one [12]-[15]. OPC, FA and GGBFS slag were treated with the above prepared solutions two and three and it was found that cement and slag were completely dissolved in solutions two and three and FA sample does not participate any dissolution with solutions two and three [12]-[15]. Thereafter, method was studied with OPC+PI, PPC, PSC and CC and studied in three stages.

- Stage one: Study the selective dissolution on pure OPC sample
- Stage two: Study the selective dissolution on PPC and PSC samples
- Stage three: Study the dissolution on CC samples

125 ml of EDTA (0.05M) and 125 ml distilled water were taken into the beaker and added 15 ml of TEA (1:1 ratio solution). Finally, the resultant solution was adjusted to 11.6 ± 0.1 pH by adding 0.1M NaOH. Thereafter, 0.25 gms (S) of representative sample is going to be added to the resultant solution and placed on the magnetic stirrer for 30 mins [4], [12]-[15]. After stirring for 30 mins of resultant solution at ambient temperature, the solution was filtered using 40 no Whatman filter paper by washing with ethanol for 5 times. The obtained residue along with the filter paper was placed

into the empty platinum crucible after noting down the weight of empty crucible as C. Then the crucible heated on the gas burner for about 20-30 mins by ensuring the filter paper removal. Then the obtained product is placed on the furnace with the temperature range of 800-900 °C for about 30 mins. The residue is called as R1. The weight of the resultant residue is measured on electrical balance.

$$\text{The percentage of cement (O\%)} = (S-R1)/S*100$$

$$\text{The percentage of slag and fly ash (SF\%)} = [(R1-C)/S]*100$$

S = sample weight; C = empty crucible weight; R1 = Crucible + residue weight.

The obtained residue (R1) is further treated to separate the slag and FA and separation of slag and FA done in two methods.

First Method: EDTA#stack solution of 125 ml was diluted to 250 ml by adding 125 ml of distilled water in a beaker and then the pH of this solution was adjusted to 11.5 ± 0.1 by adding NaOH dropwise. Thereafter, residue R1 is added to the resultant solution and placed on the magnetic stirrer for 30 mins. After stirring for 30 mins of the sample and solution, the sample is filtered using 40 no Whatman filter paper by washing with ethanol for 5 times to ensure the complete separation of residue and dissolved compositions from the beaker. The obtained residue is placed into the empty platinum crucible by noting down the weight as C along with the Whatman filter paper heating on the gas burner for 20-30 mins. Then the obtained product is placed on the furnace with the temperature range of 800-900 °C for about 30 mins. The residue is called as R2. The obtained residue R2 is weighed on the electric balance.

Second Method (Alternative Method for Residue R2): For one liter of the 2.68 N H₃PO₄: 1000 mL x 2.68N = V (mL) x 45.6 N. Thus, we measure 58.82 mL (almost 59 mL) of the stock acid and add it to 100-200 mL of water, mix it and the dilute the mixture up to one liter to have a final concentration of 2.68 N or 5% of H₃PO₄ solution. 30 mL of 5% of H₃PO₄ solution is taken in the beaker and added 30 mL of distilled water. Then the obtained residue from the above step (R1) is added to the resultant H₃PO₄ solution. Resultant solution was placed on the magnetic stirrer and then the solution was stirred about 30 mins at ambient temperature. Then the solution was filtered through 40 no Whatman filter paper by washing with ethanol several times. The obtained residue is placed into the empty platinum crucible by noting down the weight as C along with the Whatman filter paper heating on the gas burner for 20-30 mins. Then the obtained product is placed on the furnace with the temperature range of 800-900 °C for about 30 mins. The residue is called as R2. Finally, the resultant residue R2 is weighed on the electric balance [16].

The selectively dissolved weight percentage of FA constituent in the composite cement sample was calculated with the subtraction of solution one residue (R1) (which contains FA and slag) and residue (R2) of solution two or solution three from the from the total sample weight.

$$\text{The percentage of fly ash (F\%)} = [(R1-R2)/S]*100$$

$$\text{The percentage of slag} = 100 - (O\% + F\%)$$

Chemical analyses of all the cement samples were carried out and the results are given in Tables I-III. The systematic analysis of all the samples was carried out with the selective dissolution method. The concentration of the stack solutions, stirring time and pH adjustment are the crucial parameters for obtaining the accurate results. The obtained results with the selective dissolution method and theoretical mixing proportions are given in Tables IV-VII. All the cement samples show 10% of standard deviation with the percentage of respective constituent. The unknown PPC, PSC and CC samples were estimated by the selective dissolution method and it is found that the results match with the declared percentages of manufactures.

TABLE I
 CHEMICAL COMPOSITIONS OF PPC SAMPLES

Sample name	CaO	MgO	SO ₃	IR
PPC1	56.548	2.1142	2.309	8.28
PPC2	53.596	2.0184	2.188	5.27
PPC3	50.644	1.9226	2.067	6.02
PPC4	47.692	1.8268	1.946	6.77
PPC5	44.74	1.731	1.825	7.52
PPC6	42.34	1.988	1.716	30.85
PPC7	39.48	1.951	1.597	35.37
PPC8	36.62	1.914	1.478	39.88
PPC9	33.76	1.877	1.359	44.40
PPC10	30.9	1.84	1.24	48.92

TABLE II
 CHEMICAL COMPOSITIONS OF PSC SAMPLES

Sample Name	CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
PSC1	51.81	1.97	25.45	10.40	3.77
PSC2	50.52	1.93	25.95	11.05	3.57
PSC3	49.24	1.89	26.46	11.71	3.37
PSC4	47.96	1.85	26.96	12.36	3.17
PSC5	46.68	1.81	27.47	13.01	2.97
PSC6	45.39	1.76	27.97	13.66	2.76
PSC7	44.11	1.72	28.47	14.31	2.56
PSC8	42.83	1.68	28.98	14.97	2.36
PSC9	41.55	1.64	29.48	15.62	2.16
PSC10	40.26	1.60	29.99	16.27	1.96

TABLE III
 CHEMICAL COMPOSITIONS OF CC SAMPLES

Sample Name	IR	CaO	MgO	SiO ₂	Al ₂ O ₃
CC1	48.58	28.34	2.64	42.38	18.11
CC2	43.90	29.91	3.08	40.99	17.73
CC3	39.21	31.49	3.52	39.60	17.35
CC4	34.53	33.07	3.95	38.21	16.97
CC5	29.85	34.65	4.39	36.82	16.59
CC6	25.17	36.22	4.83	35.43	16.21
CC7	20.48	37.80	5.27	34.04	15.83
CC8	15.80	39.38	5.70	32.65	15.45
CC9	11.12	40.96	6.14	31.26	15.07
CC10	16.80	47.07	3.30	29.62	11.54

TABLE IV
MIXED COMPOSITIONS AND OBTAINED PROPORTIONS OF OPC AND PI

Sample Name	Mixing Proportions		Obtained Proportions	
	OPC	PI	OPC	PI
OPC1	99	1	98.01	0.99
OPC 2	98	2	97.02	1.98
OPC 3	97	3	96.03	2.97
OPC 4	96	4	95.04	3.96
OPC 5	95	5	94.05	4.95
OPC 6	99	1	98.01	0.99
OPC 7	98	2	97.02	1.98
OPC 8	97	3	96.03	2.97
OPC 9	96	4	95.04	3.96
OPC 10	95	5	94.05	4.95

TABLE V
MIXED COMPOSITIONS AND OBTAINED PROPORTIONS OF OPC AND FA

Sample Name	Mixing Proportions		Obtained Proportions	
	OPC	FA	OPC	FA
PPC1	95	5	94.05	4.95
PPC2	90	10	89.1	9.9
PPC3	85	15	84.15	14.85
PPC4	80	20	79.2	19.8
PPC5	75	25	74.25	24.75
PPC6	70	30	69.3	29.7
PPC7	65	35	64.35	34.65
PPC8	60	40	59.4	39.6
PPC9	55	45	54.45	44.55
PPC10	50	50	49.5	49.5

TABLE VI
MIXED COMPOSITIONS AND OBTAINED PROPORTIONS OF OPC AND GGBFS

Sample Name	Mixing Proportions		Obtained Proportions	
	OPC	Slag	OPC	Slag
PSC1	70	30	69.3	29.7
PSC2	65	35	64.35	34.65
PSC3	60	40	59.4	39.6
PSC4	55	45	54.45	44.55
PSC5	50	50	49.5	49.5
PSC6	45	55	44.55	54.45
PSC7	40	60	39.6	59.4
PSC8	35	65	34.65	64.35
PSC9	30	70	29.7	69.3
PSC10	25	75	24.75	74.25

TABLE VII
MIXED COMPOSITIONS AND OBTAINED PROPORTIONS OF OPC, FA AND GGBFS

Sample Name	Mixing Proportions			Obtained Proportions		
	OPC	Slag%	FA%	OPC%	Slag%	FA%
CC1	40	10	50	39.6	9.9	49.5
CC2	40	15	45	39.6	14.85	44.65
CC3	40	20	40	39.6	19.8	39.6
CC4	40	25	35	39.6	24.75	33.65
CC5	40	30	30	39.6	29.7	29.7
CC6	40	35	25	39.6	34.65	24.75
CC7	40	40	20	39.6	39.6	19.8
CC8	40	45	15	39.6	44.55	14.85
CC9	40	50	10	39.6	49.5	9.9
CC10	70	15	15	39.6	14.85	14.85

TABLE VIII
OBTAINED PROPORTIONS OF OPC, FA AND SLAG

Sample Name	OPC	Slag	FA
CC1	39.6	9.9	49.5
CC2	39.6	29.7	29.7
CC3	39.6	49.5	9.9
PPC	69.70	-	29.7
PSC	44.55	54.45	-

IV. CONCLUSIONS

Nowadays all the cement standards allow the blended cements production to reduce the clinker factor. All the international standards mentioned the defined percentages of SCMs for the same. But, the estimation of SCMs in blended cements is a challenging task and limited number of technologies are available for the same. Hence, the selective dissolution method is a good characterization technique to control the quality parameter of SCMs in the final product of blended cements. This methodology systematically dissolves minerals of OPC and GGBFs slag in the respective solutions and finally produces the residue of FA in the case of composite cement. Then, the percentage of each constituent can be calculated easily by considering the weight of sample and weight of residue at different stages. Conventionally, this methodology is a simple and adoptable one and produces the results with 10% of standard deviation with the corresponding percentage of respective constituent. The results suggest that this selective dissolution method has potential for estimation of OPC and SCMs content in different cement type samples.

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