



FUSION PREPARATION WITH LOI FOR XRF

Jose Las Navas, Navas Instruments, US, and Laura Oelofse, Rigaku, US, outline the use of in-situ weighing in the fusion of cement and clinker.

Abstract

Finished Cement samples have traditionally been analysed by a fusion method with an XRF analysis finish.

The fusion bead method offers the advantage of oxidising all elements to the oxide form regardless of their compound derivations. The improvement in analytical accuracy offered by the fusion technique makes for far better quality control and can be extended to clinkers for better kiln control as well.

Since the Lime Saturation Factor (LSF) is such a critical process control parameter, the calculation of the LSF based on fusions tends to be a great deal more accurate than that carried out using pressed pellets for analysis purposes.

Fusions must be monitored for losses associated with the oxidation of compounds to their oxide form as well as the loss of intrinsic moisture. Traditionally, the fusion process has been carried out on pre-dried and pre-ignited samples. With the advancement in automated fusion machines it is possible to take the sample on an as received basis and monitor the weight changes associated with the various losses and establish a final bead weight. The ratio of the bead weight to the initial sample weight allows the accurate calculation of the loss on fusion and can then be used to adjust the concentration values measured to the correct concentrations.

The use of the Navas Fusion Machine allows a reduction of two hours in sample preparation time and can also yield the Loss on Ignition value for the sample as part of the fusion process thereby improving the efficiency of the analysis process.

Introduction

X-ray fluorescence is widely used for the analysis of cements and process intermediates in the cement industry. Since time plays a major role in the economics of a cement plant, an efficient control system is necessary to quantitatively monitor the conversion pathway for limestone, sand and marl to clinker and for the blending of clinker with anhydrite or gypsum to form cements.

Raw meal and clinker analysis have traditionally been carried out using hydraulically pressed pellets and reading by XRF. This has been based on the assumption that the clinker output for a given kiln remains fairly constant, with small variations that can be tolerated in the 'in-type' standardisation method used to calibrate the XRF.

The fusion bead method is an effective sample preparation technique for accurate analysis of a wide variety of powder samples by XRF spectrometry such as ores, rocks and refractory materials, for it eliminates heterogeneity due to grain size and mineralogical composition. In order to obtain highly accurate results,

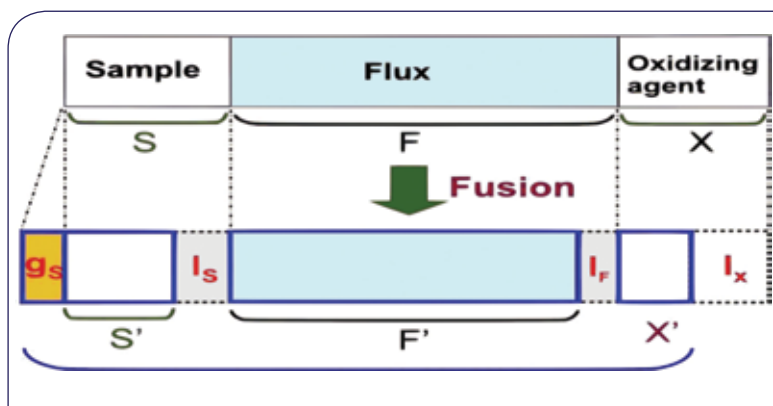


Figure 1. Weight changes in fusion.

S: sample, **B:** bead, **F:** flux, **X:** oxidizing agent, **S':** sample left in bead, **F':** flux in bead, **X':** decomposed oxidizing agent in bead, **gS:** GOI of sample, **IS:** LOI of sample, **IF:** evaporation of flux, **IX:** evaporation of oxidizing agent.

it is necessary to provide a constant flux-to-sample ratio (flux ratio) in each sample preparation definitively. Even though the weighing is performed precisely, variation in flux ratio may occur owing to loss on ignition (LOI) or gain on ignition (GOI) in samples, evaporation of flux and decomposition of oxidising agents and non-wetting agents added during fusion. These variation factors can cause analytical errors in the fusion bead method as well as introduce matrix effects.

Attempts to correct for variations in weight based on flux weight and sample weight and to correct for LOI/GOI have been applied in the calibration method to eliminate these error factors in the fusion method for ore analysis (ISO9516-1: 2003(E)), but the application of these corrections is limited and not flexible. Rigaku Corporation has established a unique, easy-to-use, universal fusion bead correction method for the empirical calibration method with matrix correction for fusion bead analysis. The advanced correction equation has been derived from the theoretical intensity equation based on the principle of X-ray absorption characteristics. The equation consists of alpha coefficients computed by a fundamental parameter (FP) method. The software computing alpha coefficients is capable of calculating coefficients for weight ratios of flux or bead to sample and oxidising agent to sample, as well as matrix effect by components in samples. It is also possible to calculate coefficients for the composition of bead that the total content exceeds 100% owing to GOI, where where oxidation of elements in samples occurs. This correction method can be used in correcting LOI/GOI, flux evaporation and variations in flux ratio due to weighing variations. We have demonstrated that the method accurately corrects these effects for iron ore and copper concentrate. For cement samples the correction algorithm does not need to take oxidising agents into consideration.

Figure 1 shows changes of component weights during fusion, which can cause analytical errors. In the model in Figure 1, weight change of the oxidising agent is also considered. For example, when sodium nitrate is added as

an oxidising agent, sodium nitrate (X) breaks down during fusion and sodium oxide (X') is left in bead, while nitrogen oxide is evaporated. X' can be obtained by simple calculation from X because the decomposition reaction of the oxidising agent during fusion is known.

The bead weight is expressed by the following equation:

$$B = F + S + X - L$$

L represents the total of LOI and GOI. When the GOI of the sample during fusion is larger than the LOI of the sample during fusion, L is a negative value. For simplicity, decomposed oxidising agent X' is expressed as X. Henceforth, in this article, X represents the decomposed oxidising agent left in bead. The weight of decomposed oxidising agent is calculated from the original weight before fusion described above.

In addition to those changes during fusion, variation of weights of sample and reagents, which causes variation of flux ratio to standard ratio, has to be included in correction factors. These correction schemes are embedded in the Rigaku ZSX software but may be available on many other XRF software platforms

Experiment

The system is made of one furnace and two precision balances of 0.1 mg readability and a PC or laptop, external and internal balances – internal inside the furnace frame – both connected to a Navas Instruments designed electronic board. The USB from the furnace is connected to a PC or laptop by USB cable for operation and data handling.

The furnace, of only 2KW 220 AC being circular, has a perfectly controlled temperature with air recirculating for greater homogeneity. The furnace has a capacity of up to 16 beads, with a maximum temperature of 1150 – 1200°C. Higher temperatures are not necessary, since flux will evaporate at 1100°C. Information including graphs and weight loss provided about flux evaporation at 1100°C can be provided upon request.

Operation of the Navas Fusion Machine

Flux used does not contain non-wetting agent.

1. The buoyancy factor for each mouldable is established once off to compensate for the weight variance at operating temperatures.
2. Operator will calibrate flux contamination (not evaporation) by fusing a bead with only flux. This is done with every new flux container.
3. Operator will prepare a set of pieces of cellulose with no ash and add 1 mg of lithium bromide for further use. This operation can be done during bead fusion; the cellulose ball is added after the bead has been fused and LOI results provided.
4. Operator places mouldable in external balance, software will take this weight.

Table 1: Using fused bead weight: Sample Ratio

	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	K2O	CaO	TiO2	MnO	Fe2O3
Unit	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
Number	10	10	10	10	10	10	10	10	10	10	10
Minimum	0.198	1.431	4.83	19.15	0.186	3.01	0.526	62.80	0.259	0.079	3.36
Maximum	0.204	1.540	4.86	19.32	0.210	3.03	0.551	63.07	0.282	0.087	3.40
Average	0.201	1.5	4.84	19.22	0.196	3.02	0.54	62.94	0.269	0.0826	3.38
Std dev.	0.023	0.022	0.01	0.05	0.009	0.01	0.007	0.084	0.007	0.002	0.010

Table 2: Using flux weight: Sample weight ratio

	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	K2O	CaO	TiO2	MnO	Fe2O3
Unit	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
Number	10	10	10	10	10	10	10	10	10	10	10
Min	0.135	1.49	4.80	19.29	0.185	3.01	0.544	62.86	0.259	0.072	3.38
Max	0.253	1.56	4.85	19.47	0.219	3.04	0.520	63.15	0.281	0.085	3.42
Average	0.200	1.52	4.84	19.39	0.200	3.03	0.528	63.00	0.27	0.08	3.40
Std.Dev	0.036	0.023	0.018	0.079	0.010	0.011	0.008	0.086	0.008	0.004	0.013
RSD (%)	15.92	1.58	0.33	0.42	5.23	0.37	1.46	0.15	2.75	5.01	0.31

- Operator adds 50% of flux. No precision flux dosing here – the exact weight will be measured automatically.
- Operator adds 500 mg of sample, no precision dosing needed here.
- Software will present the needed flux to obtain the proper ratio for example 1 - 10. Operator doses flux and observes number going down to zero, +/- 0.3 mg or better.
- The initial sample mass is recorded; the mass of flux added is recorded.
- Mouldable with sample and flux is placed in auto loader.
- Repeat the process until loader is full or there are no more samples.
- Add the job by clicking 'add' so the system will know the job is complete.

The instrument will load each one of the mouldables automatically into the furnace that is at 1050°C and start the fusion cycle.

- Mouldables will stay for about 3 – 5 minutes for the flux to melt.
- Mouldables will be inclined (with a patent pending system) and occasionally agitated by rotation and reverse operation of the ceramic carousel that holds the mouldables. This dual agitation and mixing system provides very homogeneous beads.
- Simultaneous to the fusion process, weights are taken inside the furnace on every mouldable until the programmed time has expired. Those weights indicate if any flux evaporation has occurred (normally none). LOI on the sample and final bead weight calculated as flux minus sample minus LOI

taking into consideration moldable buoyancy and flux contamination weight loss.

- After the LOI result is obtained, the furnace plug will open and a paper ball with lithium bromide of only 1 mg (or other non-wetting agent) is added. Operator places one ball at a time using tongs inside the mouldables that are just below the furnace ceramic plug. The carousel rotates at every addition, ensuring the uniform release of the fused bead from the surface of the platinum mouldable.
- Beads come out automatically from the auto loader for cooling.
- No mouldable cleaning needed. The mouldables can be reused again as they are perfectly clean. No residues are left in the mouldable after fusion.

Beads are measured by XRF and the weights of the sample and flux or the weights of the sample and final



Navas 5000 instrument.

bead weight can be entered and made available for XRF calculations.

To show the efficacy of the approach used by the Navas Fusion Maker, 10 replicate beads of the same Portland cement were made and read on a Rigaku Supermini 200 using the two different correction approaches. The replicate results were compared for each element measured for low and high readings and an average was calculated. A measure of the spread of the data was then made to see how well the replicates agreed with one another. In the second set of data a uniform sample to flux ratio was assumed as would be the case with all other commercially available fusion machines and the standard deviation for each replicate set was calculated. This was repeated, but this time the actual catch weights of the sample and the final bead weight were entered into the XRF program and the standard deviation of the first set of data was compared to the second set.

From the data presented on the previous page it can be clearly seen that the use of the sample weight/final bead weight ratio gives more precise values for the analysis as evidenced by the smaller RSDs for every element.

The spread in the data evident in the second experiment is due to the assumption that the sample/flux ratio remains constant, which is not the case. There are small losses of flux and of non-wetting agent that happen in a non-uniform way during the fusion and thus one cannot adjust for these losses unless a measurement of the final bead weight is taken and used in the correction term.

Conclusion

The Navas Fusion system provides users with a unique ability to weigh the sample into the crucible and record the weight. The bead weight is measured in situ in the furnace. These data sets are available for input into the relevant XRF software to automatically correct for these small changes in the sample/flux ratio, allowing for more precise and ultimately better accuracy of analysis.

The fact that it is not necessary to pre-dry the sample as the LOI factor is determined in situ in the furnace at the time of the fusion saves meaningful amounts of time and allows for highly precise analysis to be carried out with greater precision and ultimately better accuracy. The elimination of crucible cleaning in the Navas mouldable configuration (a must in the crucible-casting mould combination) makes operation of this fusion system extremely simple, increases the convenience associated with the fusion preparation and saves substantial amounts of time. 🌐

Bibliography

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