Assessment of Use of
Air Cooled Steel Slag / Granulated Slag
as Raw Mix Corrective in Cement Manufacture

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SUMMARY & CONCLUSION

I. The compositional parameters of Air cooled Steel Slag & GGBS – SF are compositionally compatible for their use as corrective in cement manufacture .

II. Air cooled Steel Slag & GGBS – SF have lower fusion temperatures which

- **Produces liquid earlier to the clinker liquid formation temperature of Raw Mix**
- **Accelerates the clinkering reactions especially occurring post liquid formation**
- **Enhances the rate of C_3S formation.**
- **Improves the Burnability of Cement raw Mix**

III. Depending up on compositional parameters of Raw materials as well as slag , use of these slags could

- **Reduce Consumption of high grade limestone or would increase the consumption of Low / marginal grade Limestone**
- **Lowers/alters the consumption of aluminous / ferruginous Corrective Materials**

IV. The advantages of use of these slags is more pronounced for the Raw Mixes having higher A/F ratios .

V. In general the quality of OPC with use of slag as corrective is better than that of Raw Mix without use of Slags as corrective

Thus considering all the above aspects use of ACSS or GGBS – FS as Raw mix component would be most advantageous

Assessment of use of Air cooled Steel Slag /Granulated Blast Furnace Slag as Corrective in Cement Raw Mix

1.0 Introduction:

Air cooled steel slag (**ACSS**) generated During Steel manufacturing process is very hard & difficult to grind in nature & is highly crystalline in nature & so cannot be used as MIC in Slag cement manufacture. However, the compositional parameters of various steel slag collected from different sources indicates that these slags are normally richer in CaO content with relatively lower SiO_2 & higher in Fe_2O_3 contents compositionally could suit as alternative material . In view of this to assess feasibility of use of ACSS as corrective, comprehensive studies were under taken at RMPD dept. of Quality & Product development Division. The details of studies carried out for assessing the feasibility of use of ACSS are summarised below

- Characterization of Air Cooled Steel Slag
- Raw Mix Design Studies using Kymore Plant Raw Materials with and without slags
- Comparative assessment of Reactivity of Raw Mixes with the presently used correctives used at Kymore and with use of Air Cooled Steel slag, Granulated slag

2.0 Characterization of Air Cooled Steel Slags:

The detailed analysis data of Compositional parameters, Mineralogical characteristics , Micro-structural features & Melting Characteristics on various steel slag collected from different sources is presented below

2.1 Compositional Parameters:

Compositional parameters of the Air cooled Steel Slag is summarised below.

% Oxides	Durgapur			Bokaro		MUSCO		Jindal			
	1	2	3	1	2	1	2	1	2	3	4
SiO_2	24.5	14.8	15.2	9.3	8.8	14.8	13.9	12.8	13.5	13.4	12.5
Al_2O_3	5.5	1.4	1.5	11.8	12.0	16.9	15.5	1.3	1.5	1.3	1.3
Fe_2O_3	19.7	25.6	27.8	22.1	22.3	5.4	13.1	33.4	32.5	32.4	33.4
CaO	37.1	48.3	45.0	41.9	42.2	39.2	34.3	43.6	44.0	44.4	43.6
MgO	3.8	4.5	4.8	5.1	5.0	9.9	12.2	5.2	5.3	5.2	5.2
LOI	Gain	Gain	0.3	0.4	0.6	9.5	6.2	0.1	0.1	0.1	Gain
Na_2O	0.13	0.16	0.16	0.08	0.09	0.06	0.15	0.01	0.01	0.01	0.01
K_2O	0.20	0.06	0.07	0.17	0.20	0.02	0.06	0.03	0.07	0.03	0.03
SO_3	0.1	0.1	0.1	0.3	0.30	0.8	0.6	0.5	0.01	0.1	0.5
Cl	0.004	0.007	0.005	0.013	0.013	0.007	0.008	0.005	0.007	0.008	0.007
TiO_2	1.1	0.9	0.9	0.4	0.40	0.39	0.34	0.04	0.6	0.6	0.6

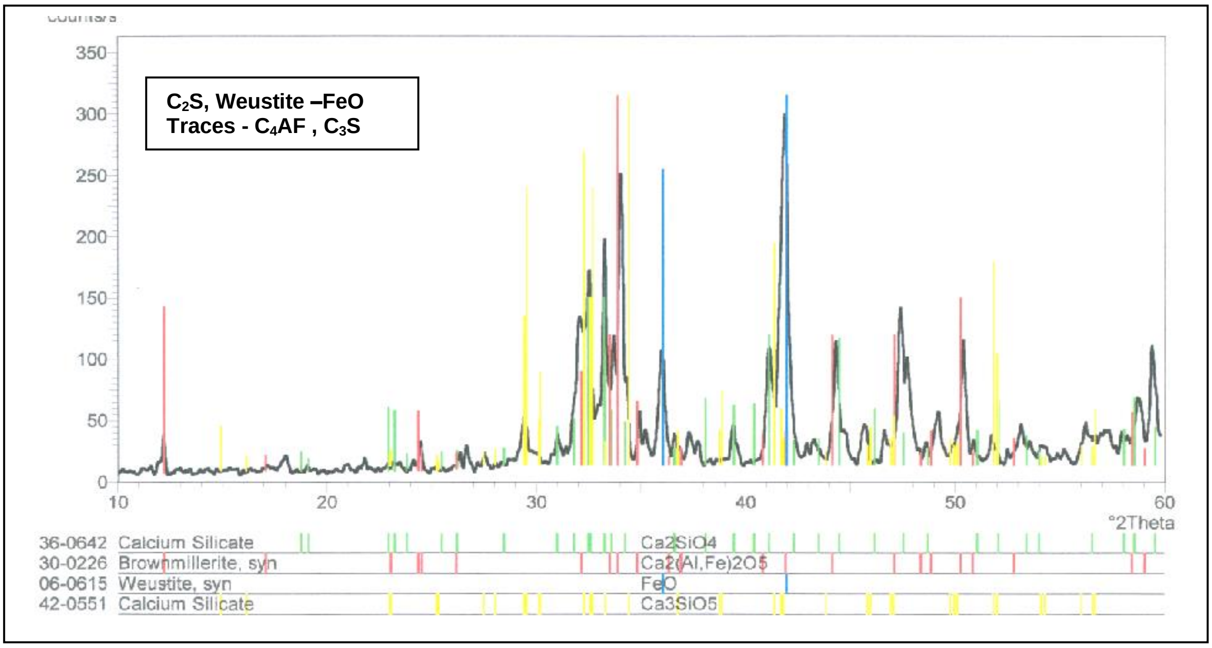
The above data indicates that irrespective of sources the Air Cooled Steel Slags are richer in CaO (37.1% to 48.3) with lower SiO_2 (8.8% to 24.5%). Considering the higher CaO & lower SiO_2, the ACSS are compositionally suitable as CaO bearing material, especially in plants where limestone deposits are marginal like Chaibasa Plant, this could also be advantageous it would also help decreasing high grade limestone usage in Plants. The other compositional advantage of use of ACSS is that it is richer in Fe_2O_3 content, thus the use of ACSS would reduce the consumption of Ferruginous corrective.

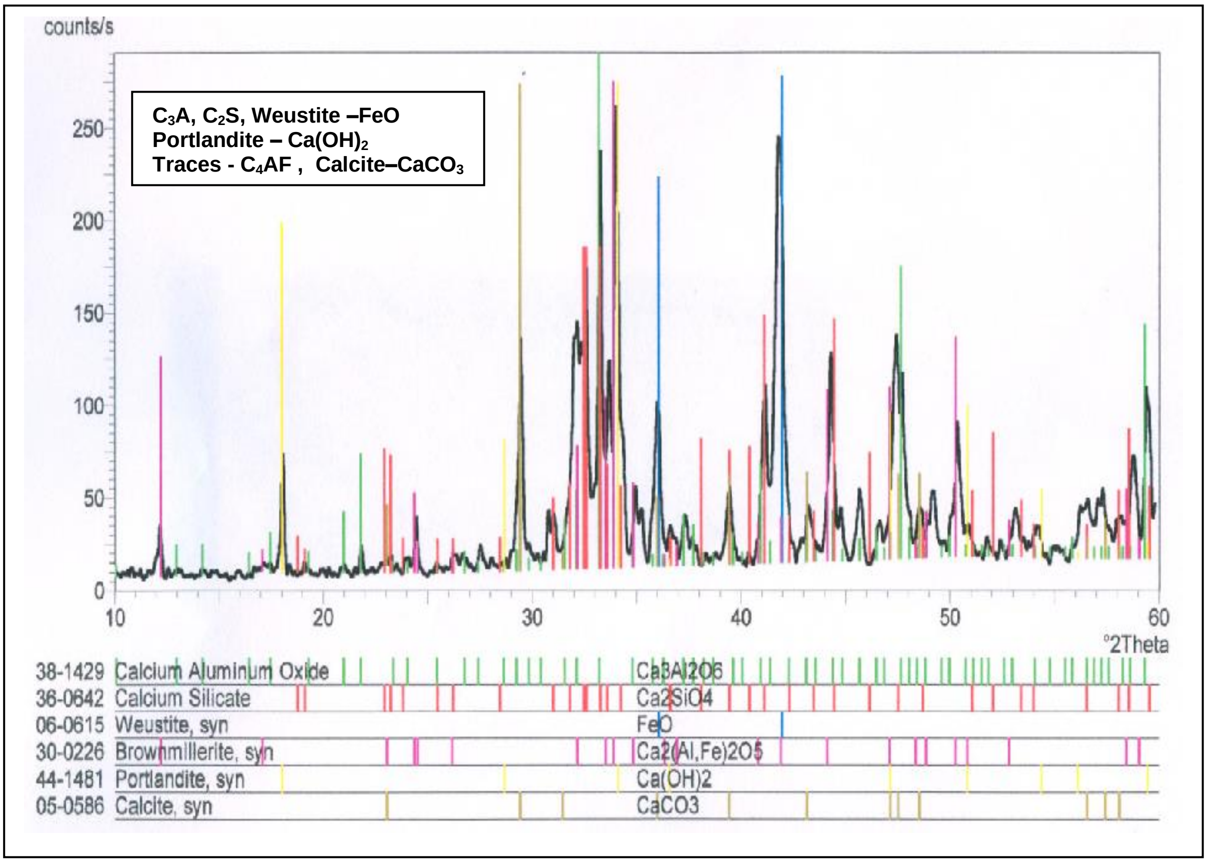
The preliminary Raw Mix design calculations for various type of Raw materials & Limestone quality available across the country had indicated that, ACSS up to 2 to 4% could be used conserving high grade limestone consumption, more over the use of ACSS could also help in reducing consumption of Ferruginous corrective. However % usage of this would be function of chemical compositional/variability in composition of ACSS as well as Raw Materials composition of that Plant.

2.2 Mineralogical Characteristics :

The minerals identified in the ACSS are more or less similar, typical XRD scans are enclosed for ready reference

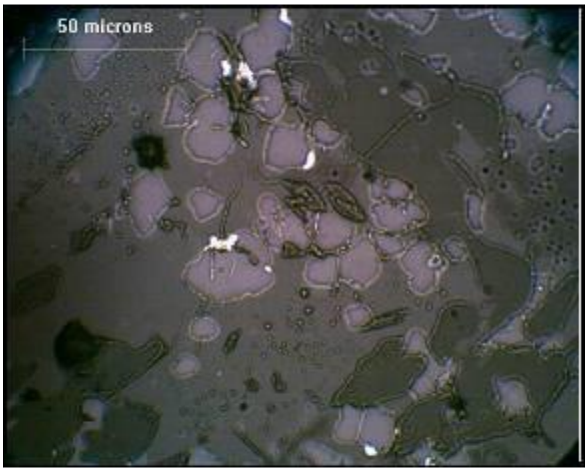
XRD of Air Cooled Slag indicates presence Major Minerals like **dicalcium silicate (Ca_2SiO_4), Dicalcium ferrite, Wustite (FeO), Porlandidte ($Ca(OH)_2$), Lime (CaO) and Rankinite ($Ca_3Si_2O_7$)** .

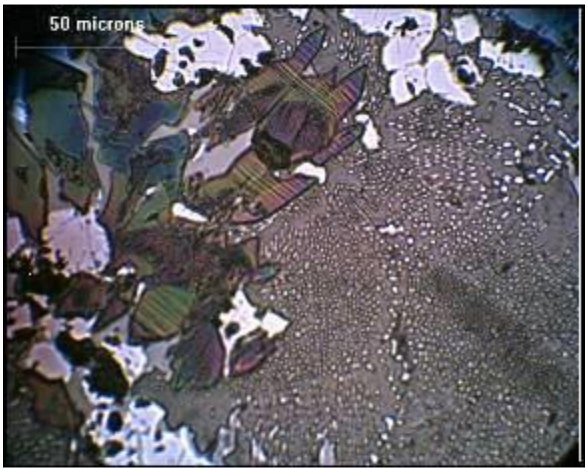




2.3 Micro-Structural Features

Polished mounts of Air cooled slags under Reflected light Microscopy technique indicates by and large Slags are highly glassy and chemically reactive with presence of minerals like **Alumino-ferrite, Ca-aluminates & Ca – Mg –Silicates**





2.4 Fusion Characteristics of Air Cooled Steel Slag :

Melting behavior of Air Cooled Steel Slag studied with heating Microscopy, expectedly Slags have more or less similar melting characteristics as ummarized below

- No Change Upto 1200 ^{0} C.
- Slow Shrinkage 1240 TO 1260 ^{0} C
- Rapid Melting Starts at 1270 ^{0} C
- Melting Range 1270 TO 1300 ^{0} C .
- Liquification At 1300 TO 1320 ^{0} C
- Complete Liquification At 1320 ^{0} C

Thus the fusion Characteristics of Air Cooled Steel Slags indicates that use of these slags as Raw mix component expected to

- **Produce liquid earlier to the clinker liquid formation temperature of Raw Mix**
- **Accelerate the clinkering reactions especially occurring post liquid formation**
- **Enhances the rate of C_3S formation**

To assess the effects of use of ACSS as corrective, detailed studies were under taken with Raw Materials from Kymore Works.

3.0 Feasibility studies on Use of Air cooled Steel Slag / Granulated Slag as corrective

For assessing the effect of use of Air cooled Steel Slag (ACSS) / granulated slag, as corrective with ACC Kymore Plant Raw Materials,.

Air Cooled Steel Slag from Jindal Steel was considered along with Raw materials from ACC Kymore for the studies . Raw Mix was also designed with use of Granulated slag (GGBS-SF) from M/s Sunflag Salg available at Kymore Plant .

The feasibility studies for use of Air Cooled Steel Slag / Granulated Slag comprised of

- **Characterization of Raw Materials and slags used**
- **Raw Mix Design Studies with presently used correctives (without use of slags) and with use of ACSS & Granulated slag.**
- **Comparative Assessment of Reactivity of Raw Mixes with presently used correctives and with use of ACSS and granulated slag.**

The comparative studies involved :

- Determination of Heat of reaction (ΔH) of Raw mixes by simultaneous **DSC –TG technique.**
- Comparison of Thermal behavior of Raw Mixes (with ash) with temperature, using the internal method of Shrinkage Expansion Studies developed and used at Thane labs to assess comparative raw Mix reactivity with increasing temperature .
- Comparative Lime combinability of Raw Mixes with Temperature as well as comparative Burnability.
- Comparison C_3S formation at various temperature for the raw mixes with & without use of ACSS and granulated slag.

3.1 Characterization of Raw Materials

The Raw materials received from the Cement Plant were evaluated for Chemical composition, where as the Air Cooled Steel Slag was evaluated for compositional parameters, Melting Characteristics & mineralogy by XRD.

3.1.1 Chemical Composition

The compositional parameters of Raw Materials received from Kymore & Air Cooled Steel Slag from is presented below

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LOI	Na_2O	K_2O	SO_3	Cl
White shaley material	42.7	11.4	5.7	17.1	1.6	19.3	0.06	1.54	0.04	0.01
Black shaley material	27.8	4.0	1.9	25.3	11.2	27.6	0.06	1.13	0.36	0.018
Purchased high grade	5.5	0.9	0.5	50.3	1.5	40.7	0.01	0.16	0.04	0.013
Reclaimed	10.3	1.7	10.0	44.9	3.1	38.3	0.01	0.31	0.1	0.070
Dolomite	11.5	1.6	2.1	36.2	9.4	38.1	0.02	0.66	0.03	0.009
Sandstone	75.5	10.9	3.0	1.0	0.9	5.9	0.08	1.88	0.2	0.009
Bauxite	19.9	40.1	13.1	0.4	0.15	20.0	0.07	0.17	0.1	0.007
Laterite	14.0	10.5	56.0	0.2	0.1	17.0	0.07	0.17	0.1	0.015
Blue dust	13.9	10.8	64.2	0.6	0.2	7.6	0.21	0.44	0.1	0.005
GGBS -SF	33.7	18.5	1.8	33.1	8.1	1.5	0.16	0.66	0.12	0.001
Air Cooled Steel Slag	13.5	1.5	32.5	44.0	5.3	0.1	0.01	0.07	0.01	0.001

The compositional parameter of the Raw materials & are well within the normal range of variability observed at Kymore. The observations on compositional parameters of GGBS – SF & Air Cooled Steel Slag from Jindal are summarised below

- Air cooled steel Slag is richer in CaO (44.0%) with Lower SiO_2 content of 13.5% while the granulated slag is at normally observed range of chemical composition except for relatively low alumina contents .
- The Fe_2O_3 content 32.5% in ACSS is as expected on the higher side with lower Al_2O_3 content of 1.5%.
- The minor constituents are at very low levels and are within the acceptable limits.

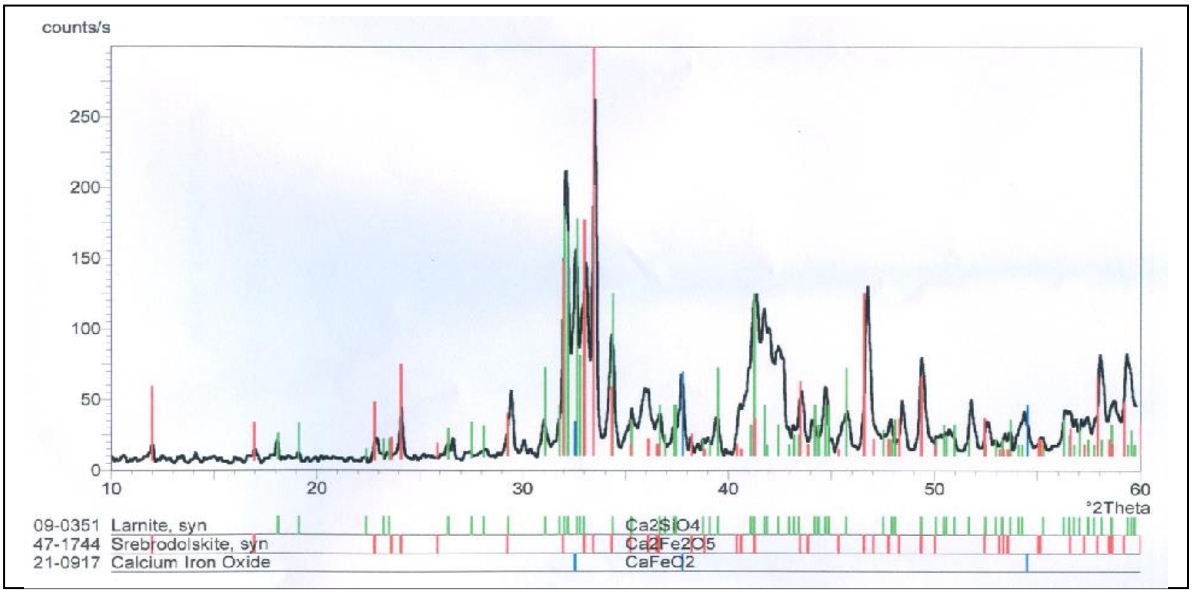
3.1.2 Melting Characteristics of Air Cooled Slag & GGBS-SF

The comparative Melting Characteristics of ACSS & GGBS-SF are given below :

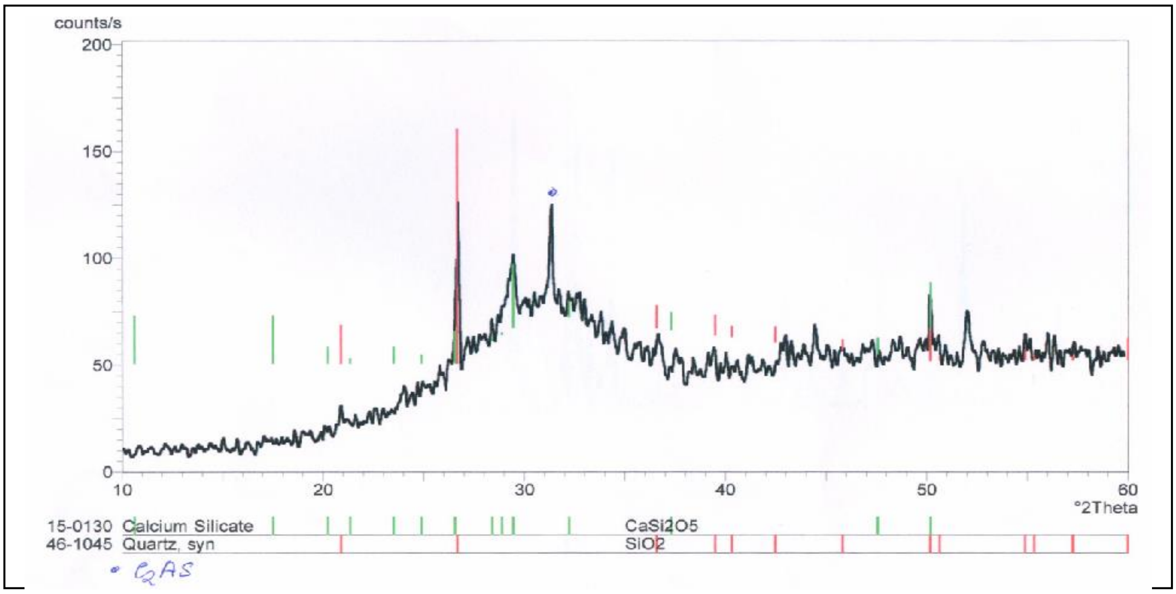
ACSS	GGBS-SF
No Change upto 1200°C	No Change Upto 11500C
Slow Shrinkage 1200 to 1300°C	Slight Shrinkage At 12200C
Rapid Melting starts at 1320°C	Slight Expansion And Bulging 1230 to 1250^{0}C
Melting range 1320 to 1340°C	**Melting Range 1260^{0}C to 1320^{0}C**
Complete Liquification at 1350°C	Complete Liquification at 13400C

The granulated slag under study has comparatively lower fusion temperature

3.1.3 Mineralogy of Air Cooled Steel Slag & GGBS-SF by XRD



XRD Scan of Air Cooled Steel Slag



XRD Scan of GGBS-SF showing predominantly amorphous nature

3.2 Raw Mix Design studies

Raw mix design studies were carried on following considerations

- Use of Raw Materials, GGBS-SF & Air cooled Steel Slag under evaluation
- Coal having Ash content of ~ 33.0% with Calorific value 4375 cals/g (as fired basis with ~ 2.0% moisture in fine coal)
- Heat of Clinkerisation 730 K Cals/kg Clinker

It may be noted that for last few years Kymore works has been regularly using GGBS as one of the corrective hence same was also considered for comparative Raw Mix Studies.

With above considerations Raw Mixes with & without use of GGBS & ACSS were selected for detailed studies targeting following Clinker parameters

✻ **Case I : Lower SM (<2.50) Higher AM (~1.65)**

✻ **Case II : Higher SM (>2.50), Lower AM (~1.45)**

	Raw mixes with high A/F of ~ 1.65						Raw mixes targeting low A/F of ~ 1.45					
Raw materials	**RX-A Without Slag**		**RX-B With 2% ACSS**		**RX- C With 1% GGBS-SF**		**RX- D Without Slag**		**RX- E With 2% ACSS**		**RX- F With 1% GGBS-SF**	
White shale	**3.9**		**3.9**		**3.1**		**4.9**		**4.7**		**4.6**	
Reclaimed Limestone	**93.2**		**92.0**		**93.0**		**92.9**		**91.8**		**92.7**	
Sandstone	**0.0**		**0.0**		**0.0**		**0.0**		**0.2**		**0.0**	
Bauxite	**1.7**		**2.1**		**1.6**		**0.6**		**0.9**		**0.1**	
Laterite	**1.2**		**0.0**		**1.2**		**1.6**		**0.4**		**1.6**	
Air cooled Steel Slag	**0.0**		**2.0**		**0.0**		**0.0**		**2.0**		**0.0**	
GGBS -SF	**0.0**		**0.0**		**1.0**		**0.0**		**0.0**		**1.0**	
	Kiln Feed & Clinker Parameters											
% Oxides	**KF**	**CL**	**KF**	**CL**	**KF**	**CL**	**KF**	**CL**	**KF**	**CL**	**KF**	**CL**
SiO_2	11.8	21.2	11.8	21.1	11.7	21.1	12.1	21.5	12.0	21.5	12.1	21.6
Al_2O_3	2.8	**5.5**	2.9	**5.5**	2.9	**5.5**	2.6	**5.0**	2.5	**5.0**	2.5	**4.9**
Fe_2O_3	2.0	**3.3**	2.1	**3.3**	2.1	**3.3**	2.2	**3.5**	2.2	**3.5**	2.1	**3.4**
CaO	42.5	64.0	42.9	63.9	42.6	63.9	42.9	63.9	42.6	64.0	42.7	64.0
MgO	3.0	**4.5**	3.0	**4.5**	3.0	**4.6**	3.0	**4.5**	3.0	**4.5**	3.0	**4.6**
LOI	37.0	0.0	36.4	0.0	36.8	0.0	36.3	0.0	36.9	0.0	36.7	0.0
LSF	1.13	**0.94**	1.13	**0.94**	1.13	**0.94**	1.12	**0.93**	1.12	**0.93**	1.12	**0.93**
MS	2.41	**2.41**	2.39	**2.39**	2.37	**2.37**	2.56	**2.53**	2.54	**2.52**	2.62	**2.59**
MA	1.38	**1.64**	1.39	**1.65**	1.40	**1.66**	1.17	**1.43**	1.17	**1.43**	1.18	**1.45**
C_3S		**50.2**		**50.3**		**50.2**		**50.2**		**50.2**		**50.7**
C_2S		**22.9**		**22.6**		**22.6**		**23.8**		**23.8**		**23.6**
C_3A		**8.9**		**8.9**		**9.0**		**7.3**		**7.4**		**7.3**
C_4AF		**10.1**		**10.1**		**10.1**		**10.6**		**10.7**		**10.4**
Liquid at 1450^0C		**29.2**		**29.3**		**27.5**		**26.2**		**26.3**		**25.9**

1.0 Assessment of Reactivity of Raw Mixes without & with ACSS and GGBS-SF:

Comparative assessment of Reactivity of Raw Mixes involves

- Assessment of Burnability
- Determination of Heat of reaction (ΔH) of Raw mixes by simultaneous **TG-DSC technique**
- Comparison of Thermal behavior of Raw Mixes (with ash) with temperature using, Shrinkage Expansion Studies developed and used at Thane labs to assess comparative raw Mix reactivity with increase in temperature .
- Rate of C_3S formation at various temperature (by XRD) for the Raw Mixes without & with ACSS & GGBS-SF
- Interrelationship of Lime release, Lime Combinability with thermal behavior as assessed by %Shrinkage/Expansion of Raw Mixes with increasing temperatures
- Interrelationship between % Shrinkage/Expansion and C_3S formation
- Microscopic evaluation of Clinkers
- Quality of OPC from Pilot scale Clinkers

All the above tests are useful for comparing the reactivity of the different Raw mixes

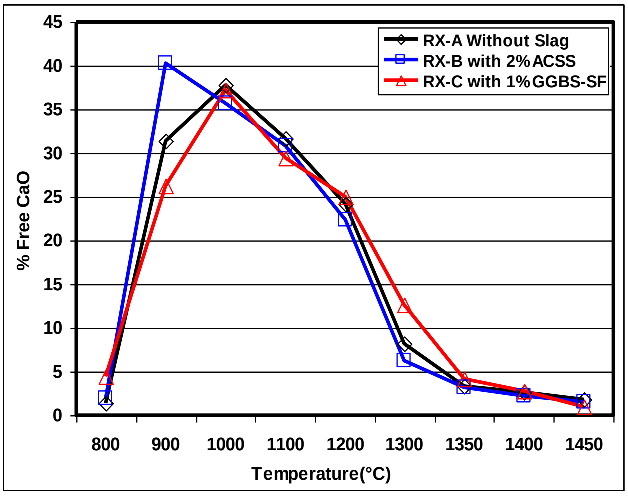
4.1 Assessment of Burnability of the raw Mixes

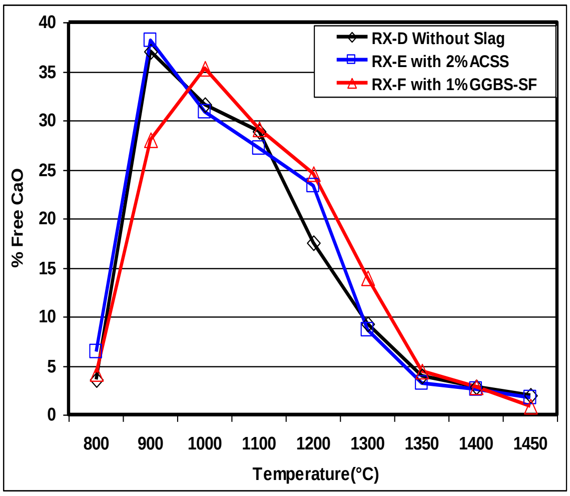
Burnability Test carried out procedurally , determines % Free CaO as well as Lime Combining ability (Lime Combining ability LC = (Total CaO – Free CaO)x100 / Total CaO), higher the lime combining ability higher is the reactivity of the Raw Mix .

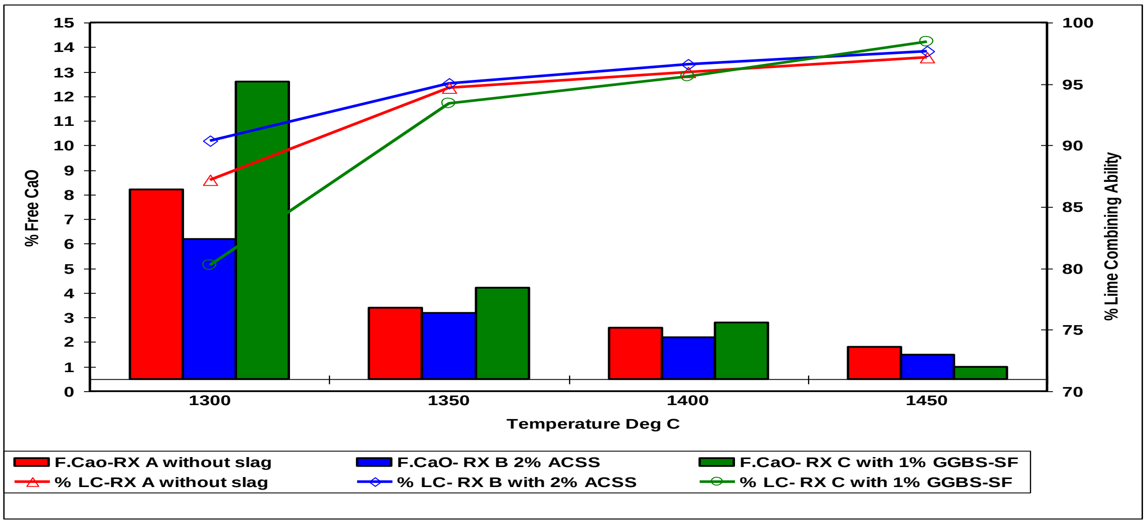
The data on Burnability Test for Raw mixes is presented below

<table>
<tr><td></td><td colspan="18">Raw mixes targeting high A/F of ~ 1.65</td><td colspan="18">Raw mixes targeting low A/F of ~ 1.45</td></tr>
<tr><td></td><td colspan="6">RX A
Without slag</td><td colspan="6">RX B
With 2%ACSS</td><td colspan="6">RX C
With
1%GGBS-SF</td><td colspan="6">RX D
without Slag</td><td colspan="6">RX E
With 2%ACSS</td><td colspan="6">RX F
With
1%GGBS-SF</td></tr>
<tr><td></td><td colspan="36">Clinker Modulii Parameters</td></tr>
<tr><td></td><td colspan="2">LSF</td><td colspan="2">SM</td><td colspan="2">AM</td><td colspan="2">LSF</td><td colspan="2">SM</td><td colspan="2">AM</td><td colspan="2">LSF</td><td colspan="2">SM</td><td colspan="2">AM</td><td colspan="2">LSF</td><td colspan="2">SM</td><td colspan="2">AM</td><td colspan="2">LSF</td><td colspan="2">SM</td><td colspan="2">AM</td><td colspan="2">LSF</td><td colspan="2">SM</td><td colspan="2">AM</td></tr>
<tr><td></td><td colspan="2">0.94</td><td colspan="2">2.41</td><td colspan="2">1.64</td><td colspan="2">0.94</td><td colspan="2">2.39</td><td colspan="2">1.65</td><td colspan="2">0.94</td><td colspan="2">2.37</td><td colspan="2">1.66</td><td colspan="2">0.93</td><td colspan="2">2.53</td><td colspan="2">1.43</td><td colspan="2">0.93</td><td colspan="2">2.52</td><td colspan="2">1.43</td><td colspan="2">0.93</td><td colspan="2">2.59</td><td colspan="2">1.45</td></tr>
<tr><td></td><td colspan="6">% CaO = 64.0</td><td colspan="6">% CaO = 64.4</td><td colspan="6">% CaO = 64.0</td><td colspan="6">% CaO = 64.0</td><td colspan="6">% CaO = 64.2</td><td colspan="6">% CaO = 64.0</td></tr>
<tr><td></td><td colspan="3">%Free CaO</td><td colspan="3">% LC</td><td colspan="3">%Free CaO</td><td colspan="3">% LC</td><td colspan="3">%Free CaO</td><td colspan="3">% LC</td><td colspan="3">%Free CaO</td><td colspan="3">% LC</td><td colspan="3">%Free CaO</td><td colspan="3">% LC</td><td colspan="3">%Free CaO</td><td colspan="3">% LC</td></tr>
<tr><td>1300</td><td colspan="3">8.2</td><td colspan="3">87.2</td><td colspan="3">6.2</td><td colspan="3">90.4</td><td colspan="3">12.6</td><td colspan="3">80.3</td><td colspan="3">9.2</td><td colspan="3">85.6</td><td colspan="3">8.7</td><td colspan="3">86.4</td><td colspan="3">14.0</td><td colspan="3">78.1</td></tr>
<tr><td>1350</td><td colspan="3">3.4</td><td colspan="3">94.7</td><td colspan="3">3.2</td><td colspan="3">95.0</td><td colspan="3">4.2</td><td colspan="3">93.4</td><td colspan="3">3.9</td><td colspan="3">93.9</td><td colspan="3">3.2</td><td colspan="3">95.0</td><td colspan="3">4.4</td><td colspan="3">93.1</td></tr>
<tr><td>1400</td><td colspan="3">2.6</td><td colspan="3">95.9</td><td colspan="3">2.2</td><td colspan="3">96.6</td><td colspan="3">2.8</td><td colspan="3">95.6</td><td colspan="3">2.9</td><td colspan="3">95.5</td><td colspan="3">2.6</td><td colspan="3">96.0</td><td colspan="3">2.8</td><td colspan="3">95.6</td></tr>
<tr><td>1450</td><td colspan="3">1.8</td><td colspan="3">97.2</td><td colspan="3">1.5</td><td colspan="3">97.7</td><td colspan="3">1.0</td><td colspan="3">98.4</td><td colspan="3">2.0</td><td colspan="3">96.9</td><td colspan="3">1.7</td><td colspan="3">97.4</td><td colspan="3">0.9</td><td colspan="3">98.6</td></tr>
</table>

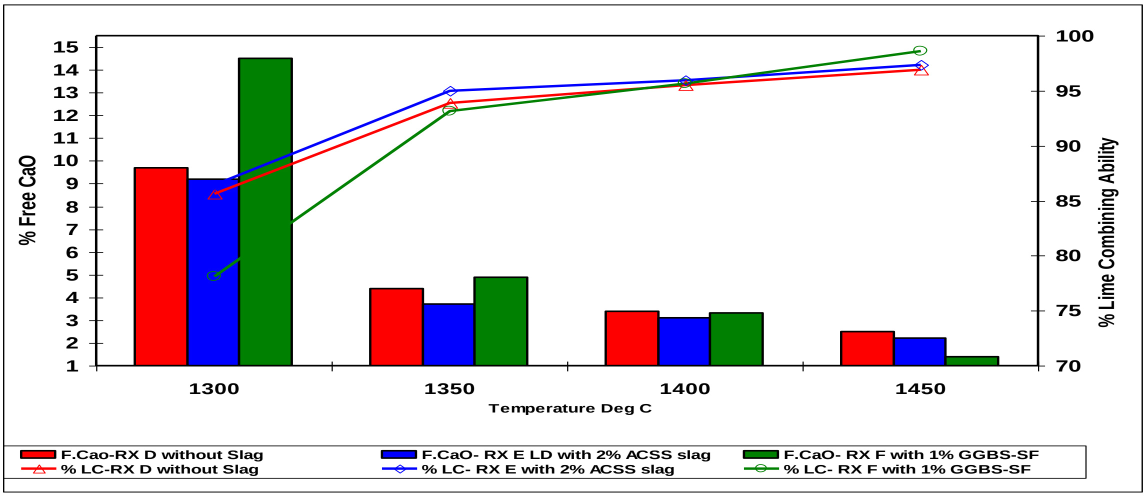
The above data indicates is graphically represented on the following page







Burnability & Lime Combining Ability of Raw Mixes at A/F 1.65



Burnability & Lime Combining Ability of Raw Mixes at A/F 1.45

The above data indicates

- The % Free CaO for the Raw Mixes with use of GGBS-SF (Raw Mix with A/F of 1.65 & 1.45) at all temperatures is lower than rest of Raw Mixes & Lime Combining ability is highest, indicating higher reactivity of GGBS-SF.
- The % Free CaO for the Raw Mixes with use of ACSS (Raw Mix with A/F of 1.65 & 1.45) at 1400^{0}C & 1450^{0}C temperatures is lower than Raw Mixes (without use of either slag) & Lime Combining ability is highest, indicating better reactivity of GGBS-SF as corrective.

4.2 Determination of Heat of reaction (ΔH) for Raw mix:

The Heat of reaction **ΔH (J/g)** of the Raw Mixes, was assessed by simultaneous Differential Scanning Calorimetry / Thermo gravimetry (**DSC –TG technique**) (Equipment **Netsch STA 409 +**)

The Experimental Conditions for determination of Heat of reaction (ΔH) are presented below

Experimental Conditions	
Sample Carrier	**:** TG-DSC with sapphire disc
Crucible	**:** Pt-Rh with pierced lids
Sample Thermocouple	**:** Type S
Purge Gas	**:** Nitrogen (50 ml/min)
Temperature Program	**:** RT – 1450°C, 10K/min

The data on Heat of Reaction (ΔH) for the raw mixes under studies is presented below

Deg.C	Raw Mixes with A/F-1.65			Raw Mixes with A/F-1.45		
	RX A Without Slag	RX B With 2% ACSS	RX C With 1% GGBS -SF	RX D Without Slag	RX E With 2% ACSS	RX F With 1% GGBS-SF
ΔH (J/g)	**1503.2**	**1403.4**	**1317.1**	**1571.6**	**1540.2**	**1401.8**

The observations on the above data are summarised below.

- **At higher Clinker A/F (1.65)** (Al_2O_3 : 5.6%, Fe_2O_3 :3.3%) the Heat of reaction for Raw Mix C (GGBS-SF) is lowest **(1317.1 J/g)** as compared to Raw Mix A without use of any Slag (**1503.2 J/g) & Raw Mix B with ACSS (1403.4 J/g)**
- **At lower Clinker A/F (1.45)** (Al_2O_3:~5.1%, Fe_2O_3:~3.5%) the Heat of reaction for Raw Mix D without use of any slag **(1571.6 J/g) is comparatively higher than ,** Raw Mix E with ACSS **(1540.2 J/g)** & Raw Mix F with GGBS-SF **(1401.8 J/g)** which is lowest. **Thus in-general use of ACSS & GGBS-SF helps in reducing the heat of reaction.**

The TG– DSC scans are enclosed in Annexure

4.3 Comparison of Thermal behavior of Raw Mixes (with ash), Shrinkage Expansion Studies of raw Mixes with temperature:

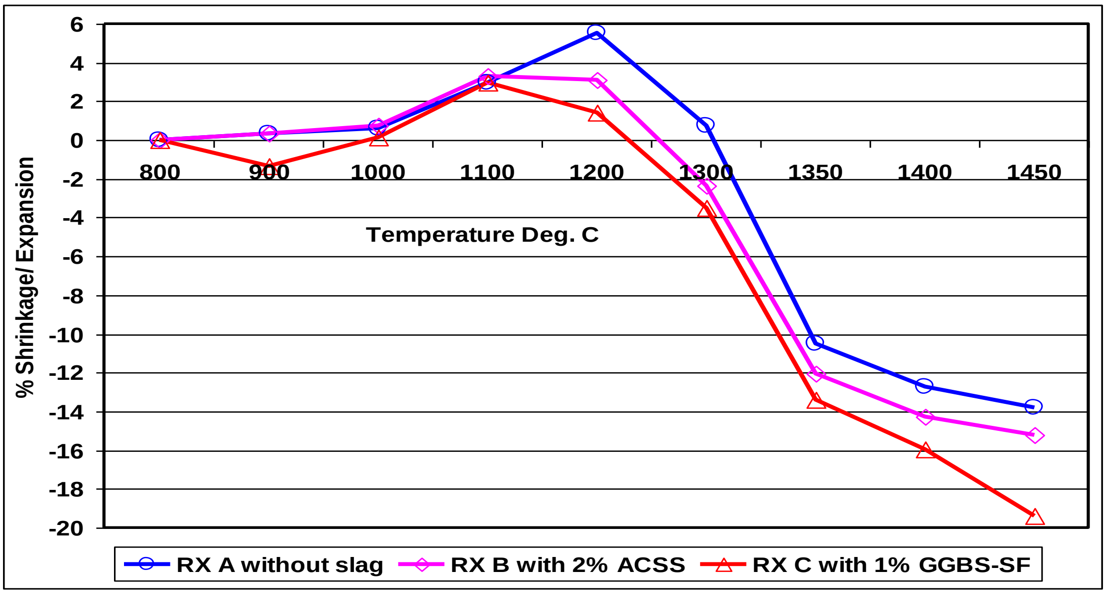
Assessment of % Shrinkage / % Expansion test of Raw Mixes with increasing temperatures was developed by ACC (R&D) earlier by carrying out series of experiments considering different Raw materials, additives, mineralisers at different raw mix /clinker modulii parameters. The test helps to assess the reactivity and thermal sineterability of the Raw Mixes with increasing temperature.

In this test Raw Mix Pellets (25.4 mm – dia. X 15mm thickness) with Coal Ash equivalent to ash absorption on clinker basis , are pressed into pellets (Pressure 500Kgs/cm^2) & fired in electrically heated high temperature furnace in temperature range from 800 to 1450^{0}C at temperature interval of 100^{0}C up to 1300 ^{0}C & at interval of 50^{0}C up to 1450^{0}C. These Raw mix Pellets were soaked for 20 minutes at each temperatures & changes in dimensions of the pellets is measured after firing at each temperature for 20 minutes .

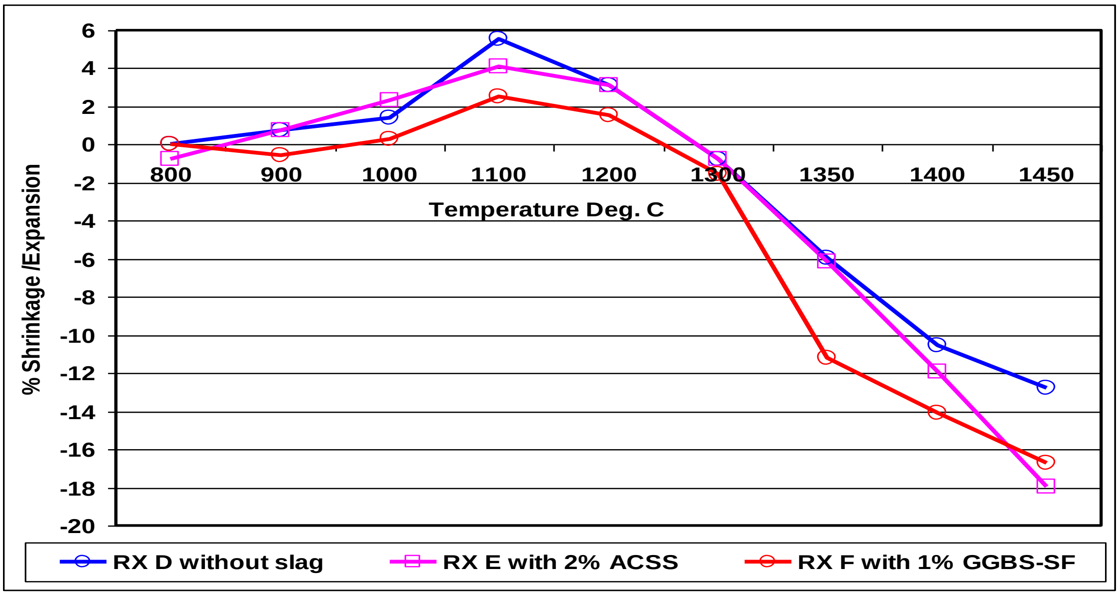
The Shrinkage expansion test predicts rate of Solid – Solid reaction/ rate of calcinations , lime combinability and rate of C_3S formation

The data on Shrinkage Expansion test for the Raw Mixes under study is presented below & also graphically depicted.

	Raw mixes with high A/F of ~ 1.65			Raw mixes targeting low A/F of ~ 1.45		
Deg.C	RX A Without Slag	RX B With 2% ACSS	RX C With 1% GGBS-SF	RX D Without Slag	RX E With 2% ACSS	RX F With 1% GGBS-SF
800	0.00	0.00	0.00	0.00	-0.78	0.00
900	0.31	0.31	-1.32	0.78	0.78	-0.55
1000	0.62	0.78	0.15	1.40	2.35	0.31
1100	2.98	3.29	2.98	5.52	4.08	2.50
1200	5.52	3.13	1.40	3.13	3.13	1.56
1300	0.78	-2.32	-3.47	-0.78	-0.78	-1.55
1350	-10.53	-12.07	-13.38	-5.98	-6.13	-11.19
1400	-12.72	-14.24	-15.96	-10.53	-11.92	-14.10
1450	-13.81	-15.25	-19.42	-12.79	-17.95	-16.75



% Shrinkage / Expansion Studies at Raw Mix A/F 1.65



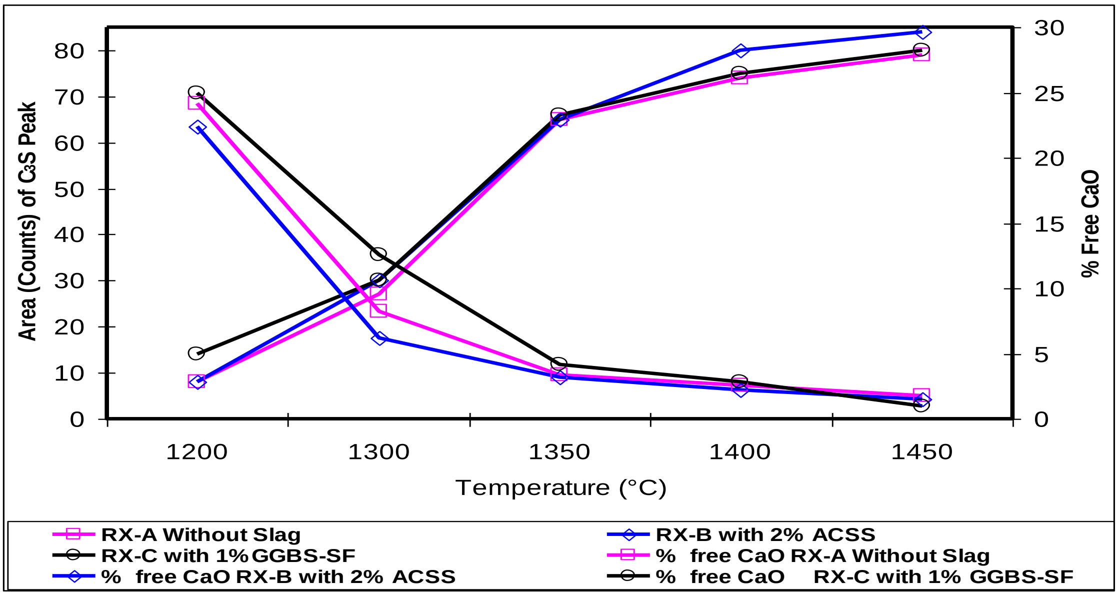
% Shrinkage / Expansion Studies at Raw Mix A/F 1.45

- The temperature Zone 800^{0}C to 1100^{0}C rate of Calcination
- The Temperature zone 1100^{0}C to 1300^{0}C indicative of extent of solid-solid reaction
- The Temperature zone 1350^{0}C to 1450^{0}C illustrates the nature & temperature of liquid formation & subsequent phase diffusion reactions forming the higher lime silicates.

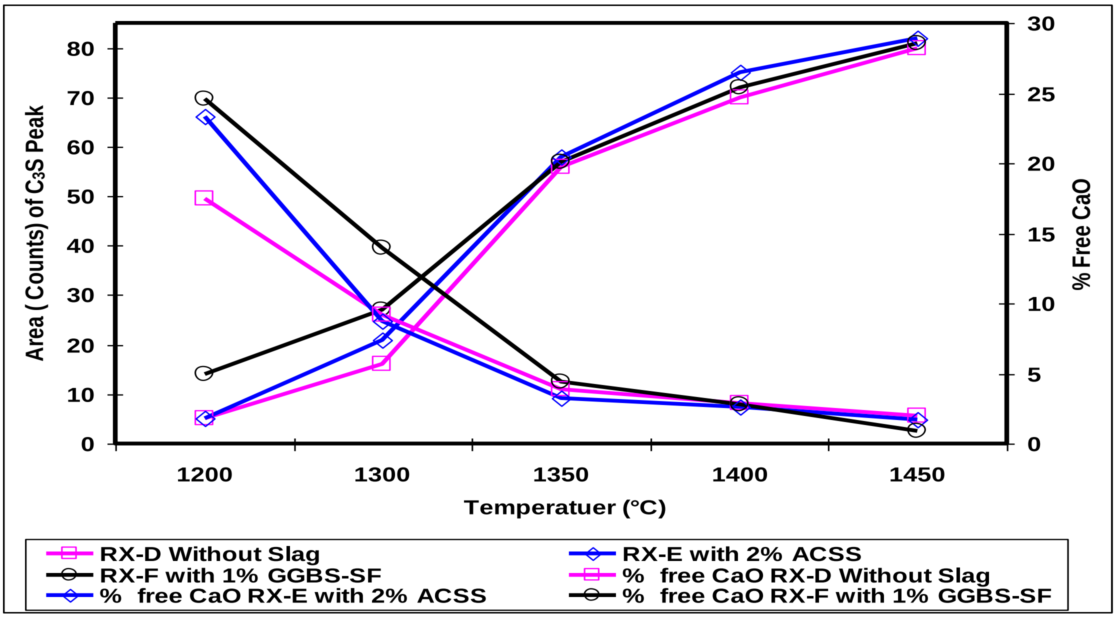
The above data indicates that with use of ACSS / GGBS-SF there is marked difference in the Shrinkage profile beyond 1300^{0}C indicating better Sinterability irrespective of A/F levels indicating - higher Phase formation/Phase assemblage post liquid phase formation , as compared to without use of slags.

4.4 Rate of C_3S formation at various temperature (by XRD) for the Raw Mixes without & with ACSS & GGBS-SF :

Rate of C_3S formation (interms of the area counts of C3S peak , at various temperature (by XRD) for the Raw Mixes without & with ACSS & GGBS-SF is depicted below :



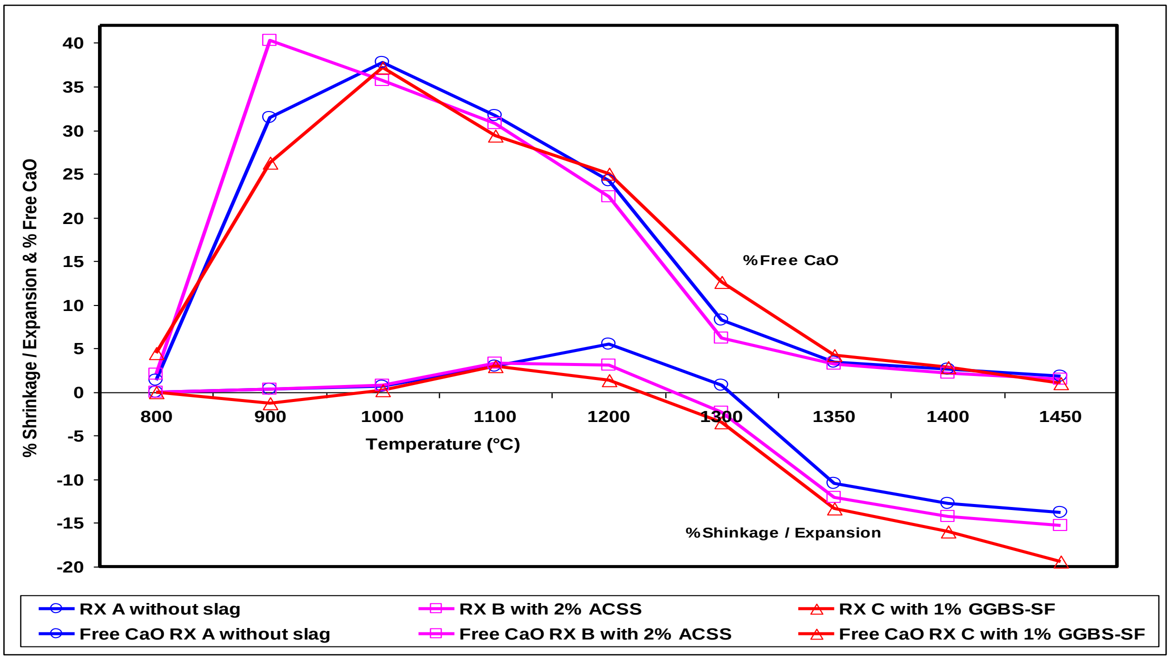
Rate of C_3S formation at various temperature (by XRD) for the Raw Mixes without & with ACSS & GGBS-SF at A/F 1.65



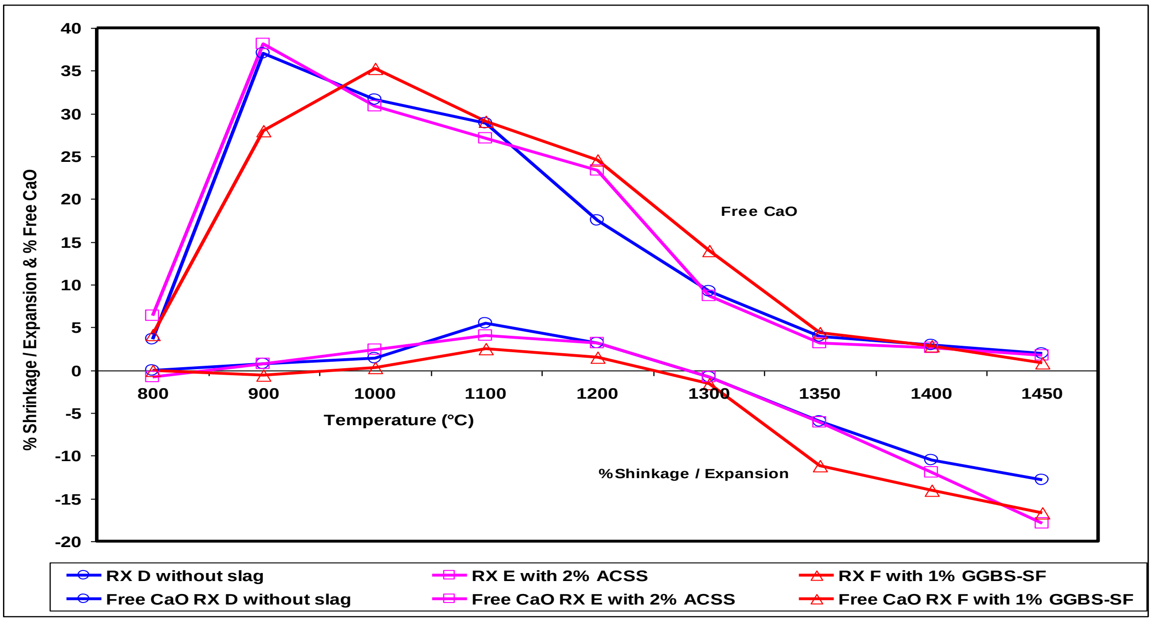
Rate of C_3S formation at various temperature (by XRD) for the Raw Mixes without & with ACSS & GGBS-SF at A/F 1.45

4.5 Interrelationship of Lime release, Lime Combinability & %Shrinkage/Expansion of Raw Mixes:

The Interrelationship of Lime release, Lime Combinability & %Shrinkage/Expansion of Raw Mixes is shown below



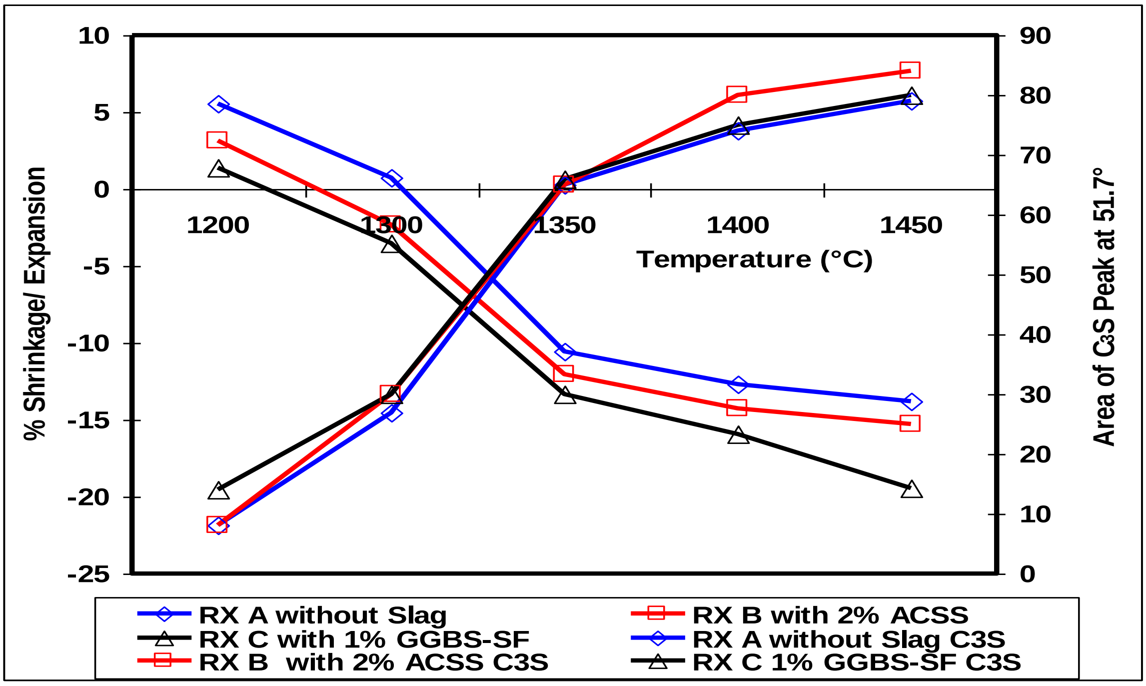
Interrelationship of Lime release, Lime Combinability & %Shrinkage/Expansion of Raw Mixes at A/F 1.65

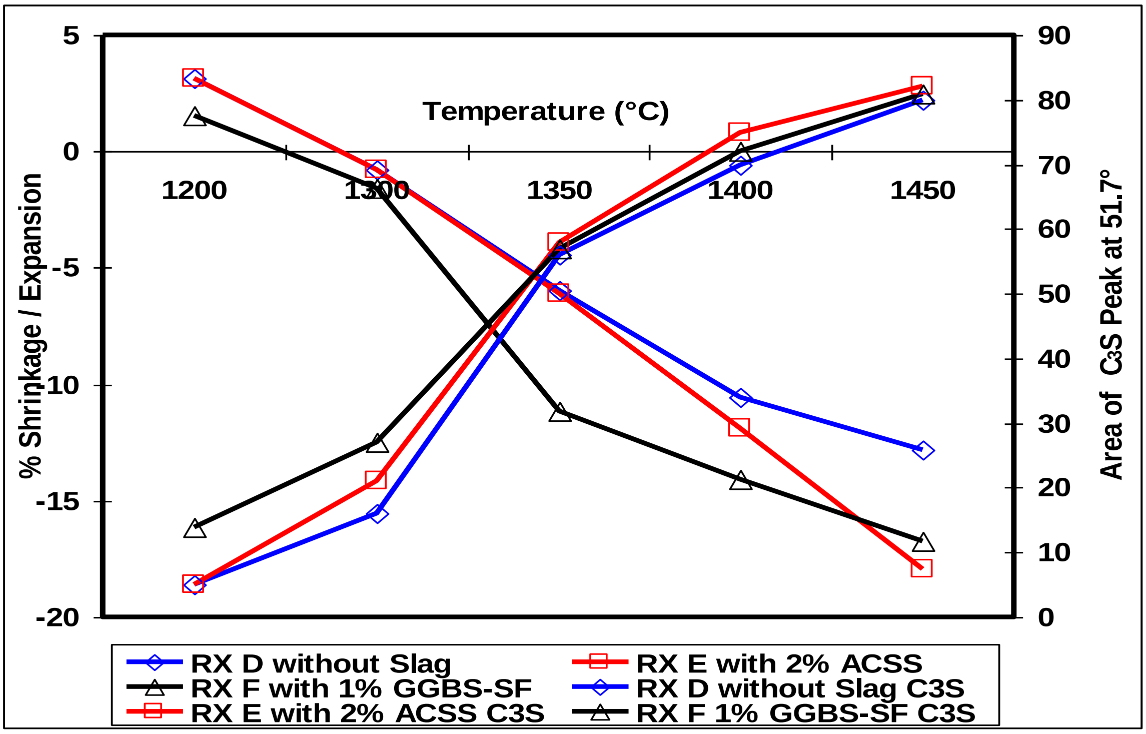


Interrelationship of Lime release, Lime Combinability & %Shrinkage/Expansion of Raw Mixes at A/F 1.45

4.6 Interrelationship between % Shrinkage/Expansion and C_3S formation:

The interrelationship between % Shrinkage/Expansion & C_3S formation is depicted below





The observations on Rate of C_3S formation (by XRD) Interrelationship of Lime release, Lime Combinability & % Shrinkage/Expansion & Interrelationship between % Shrinkage/Expansion and C_3S formation for the Raw Mixes without & with ACSS & GGBS-SF , indicates that

- **By and Large the reactivity of Raw Mixes with use of Slag shows significant improvement as compared to Raw mixes without Slags as corrective**
- **The effect of use of the slags as corrective is more pronounced at A/F ratio of 1.65 as compared to A/F of 1.45**
- **Considering the higher MgO & well established fact that for better reactivity & better strength development Al_2O_3 in Clinker has to be targeted at ~5.5% . Thus above observations of better reactivity of Raw mixes commensurate with observed better reactivity at higher A/F**

5.0 Mineralogy of Clinkers:

5.1 Evaluation of clinker from Raw mix without Slag & with 2% ACSS , 1% GGBS-SF at A/F= 1.65 for the assessment of microstructure and product characteristics (size and quantity of clinker phases)

Phases Present	C_3S, C_2S, C_3A, C_4AF, Free lime, & Periclase
Morphology of Alite	Mostly well developed euhedral to subhedral crystals with rectangular, hexagonal & prismatic shaped.
Morphology of Belite	Rounded to sub rounded & irregular crystals. Mainly as open clusters

Size and Quantity of Clinker Phases

Parameter	Unit	Test results			Small/low	Medium	Large/high
		RX – A Without Slag	RX – B with 2% ACSS	RX – C with 1% GGBS-SF			
Alite content	%	High	High	High	< 50	50 - 60	> 60
Belite content		Low	Low	Low	< 20	20 - 30	> 30
Aluminates content		High	High	High	< 4	4 - 8	> 8
Ferrite content		Medium to high	Medium to high	Medium to high	< 4	4 - 8	> 8
Free lime content		Medium	Low	Low	< 1	1 -2.5	> 2.5
Periclase content		High	High	High	< 1	1 – 2.5	> 2.5
Alite size	µm	Small	Small	Small	< 15	15 - 30	> 30
Belite size		Small	Small	Small	< 15	15 - 30	> 30
Aluminates size		Medium to Low	Medium to Low	Medium to Low	0 - 2	2 - 4	> 4
Belite cluster diameter		Medium to small	Medium to small	Medium to small	< 150	150 - 350	> 350
Free lime cluster diameter		small	small	small	< 100	100 - 200	> 200
Periclase cluster diameter		Medium to low	Medium to low	Medium to low	< 100	100 - 200	> 200
Cluster dist. belite-freelime		high	high	high	< 100	100 - 200	> 200

Crystal size distribution :

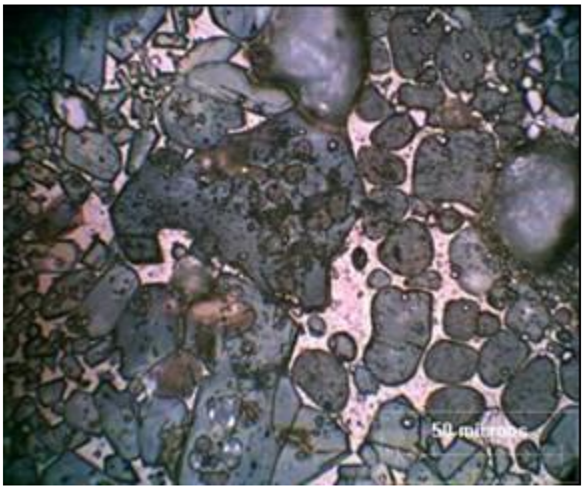
Size fraction	Unit	Free lime crystals			Alite crystals			Belite crystals		
		RX – A Without Slag	RX – B with 2% ACSS	RX – C with 1% GGBS-SF	RX – A Without Slag	RX – B with 2% ACSS	RX – C with 1% GGBS-SF	RX – A Without Slag	RX – B with 2% ACSS	RX – C with 1% GGBS-SF
0 -10 Microns	%	25.5	25.7	25.9	41.7	58.1	56.4	25.9	33.5	30.3
10- 20 Microns		68.8	43.4	55.2	48.8	37.8	39.4	58.5	62.3	58.7
20 - 30 Microns		5.7	29.6	11.8	7.7	3.4	4.1	14.3	4.1	10.1
> 30 Microns		0	1.3	7.1	1.9	0.7	0.2	1.4	0.1	0.6
Maximum size	µm	28	36	36	68	35	38	47	34	32
Minimum size		2	1	2	1	1	1	2	2	2
Average Size		13	16	15	12	10	10	14	12	13

QEP (Quantitative Estimation of Phases) (Weight % Normalised to 100)

	RX – A Without Slag	RX – B with 2% ACSS	RX – C with 1% GGBS-SF
C_3S	64.3	65.5	64.7
C_2S	19.8	19.9	19.9
Matrix (C_3A + C_4AF)	20.8	20.1	20.8
Free lime	1.4	0.9	0.9
Periclase	3.7	3.6	3.7

<u>OTHER FEATURES:</u>

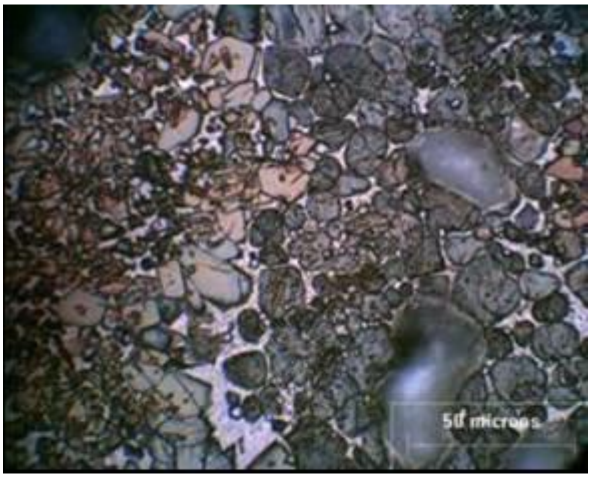
- Small Alite size, medium size widely distributed free lime & good aluminate content, may contribute towards adequate early strength potentials.
- The Alite content is good indication of high LSF, well burned nature and well adjusted kilnfeed fineness. Alite content slightly more in clinker from RX -B than clinker from RX –A , but slightly lower in clinker from RX –C in comparison with RX –B
- The average alite size is small in clinker from RX- C and RX- B compared to clinker from RX- A
- Belites are mostly multiple straitioned α' type. Most of belite clusters/nest have voids (pores). The grindability is expected to be good, because of voids & pores.
- The fine to medium grained Matrix is well distributed and porosity of grain is medium to high.
- Periclase is observed as small clusters and randomly scattered, all periclase are very fine ,less than 10 micron size. Though MgO is very high, the nature of occurrence of MgO in the clinker as fine periclase crystals(<10 micron) ,indicates low soundness risk with PPC. However OPC may have soundness problem.
- Free lime was present in most grains mostly as small open clusters, most of free lime were more than 200 microns far from belite clusters. Free lime content is decreased in clinker from RX- B & C compared to clinker from RX -A.

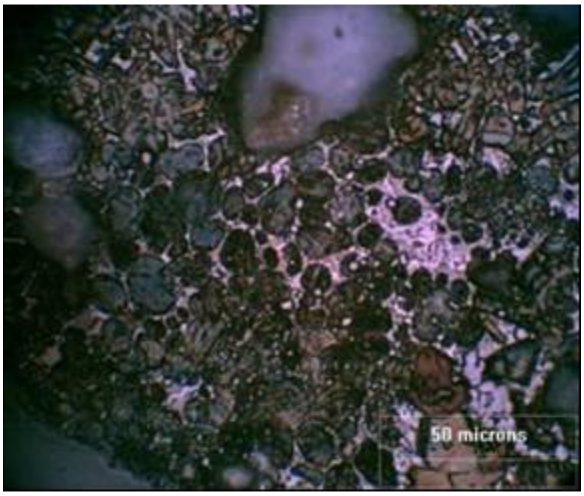


Clinker from RX A Without Slag
Well developed **euhedral alite crystals** with inclusions of belites and belite crystals in aluminate rich matrix of the clinker grains

Clinker from RX B With 2% ACSS

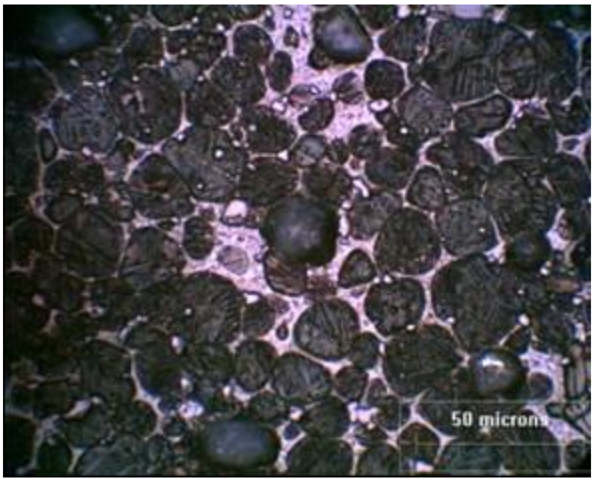
Well developed **euhedral alite crystals** with belite in aluminate rich matrix of the clinker grains





Clinker from RX C With 1% GGBS-SF

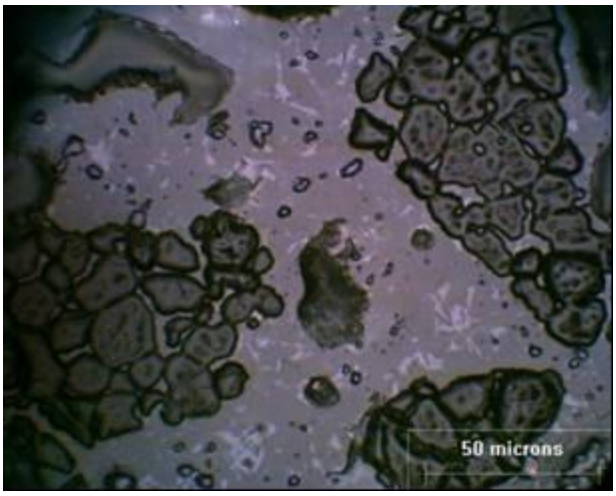
Well developed fine euhedral **alite crystals** with multiple striated belite cluster in aluminate rich matrix of the clinker grains



Clinker from RX A Without Slag
Cluster of **belites** the clinker grains indicating coarse siliceous grain in klinfeed. A majority of belite clusters has no free lime as reaction partner in its vicinity

Clinker from RX B With 2% ACSS
Well developed **belite** cluster crystals of variable sizes along with alites in aluminate rich matrix of the clinker grains

Clinker from RX C With 1% GGBS-SF
Cluster fine **free lime** with fine scattered periclase crystals grain in the clinker



Clinker from RX A Without Slag
Free lime cluster in the clinker grains indicating coarse calcite grain in kiln feed

Clinker from RX B With 2% ACSS
Well developed **small free lime cluster** along with scattered periclase in the clinker grains

5.2 Evaluation of clinker from Raw mix without Slag & with 2% ACSS , 1% GGBS-SF at A/F= 1.45 for the assessment of microstructure and product characteristics (size and quantity of clinker phases)

Phases Present	C_3S, C_2S, C_3A, C_4AF, Free lime, & Periclase
Morphology of Alite	Mostly well developed euhedral to subhedral crystals with rectangular, hexagonal & prismatic shaped.
Morphology of Belite	Rounded to sub rounded & irregular crystals. Mainly as open clusters

Size and Quantity of Clinker Phases

Parameter	Unit	Test results			Small/low	Medium	Large/high
		RX – D Without Slag	RX– E With 2% ACSS	RX– F with 1% GGBS-SF			
Alite content	%	High	High	High	< 50	50 - 60	> 60
Belite content		Low	Low	Low	< 20	20 - 30	> 30
Aluminates content		High	High	High	< 4	4 - 8	> 8
Ferrite content		Medium to high	Medium to high	Medium to high	< 4	4 - 8	> 8
Free lime content		Low to medium	Low	Low	< 1	1 -2.5	> 2.5
Periclase content		High	High	High	< 1	1 – 2.5	> 2.5
Alite size	µm	Small	Small	Small	< 15	15 - 30	> 30
Belite size		Small	Small	Small	< 15	15 - 30	> 30
Aluminates size		Medium to Low	Medium to Low	Medium to Low	0 - 2	2 - 4	> 4
Belite cluster diameter		Medium to small	Medium to small	Medium to small	< 150	150 - 350	> 350
Free lime cluster diameter		small	small	small	< 100	100 - 200	> 200
Periclase cluster diameter		Medium to low	Medium to low	Medium to low	< 100	100 - 200	> 200
Cluster dist. belite-freelime		high	high	high	< 100	100 - 200	> 200

Crystal size distribution :

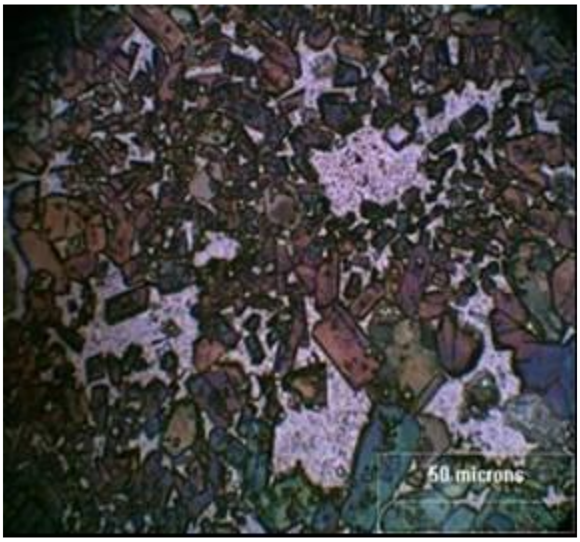
Size fraction	Unit	Free lime crystals			Alite crystals			Belite crystals		
		RX – D Without Slag	RX– E With 2% ACSS	RX– F with 1% GGBS-SF	RX – D Without Slag	RX– E With 2% ACSS	RX– F with 1% GGBS-SF	RX – D Without Slag	RX– E With 2% ACSS	RX– F with 1% GGBS-SF
0 -10 Microns	%	37.9	26.6	22.1	58.5	59.6	76.6	27.0	39.4	60.9
10 -20 Microns		52.7	70.2	65.1	37.7	36.3	21.2	62.4	49.9	38.2
20 - 30 Microns		9.4	3.2	12.8	3.4	3.2	1.5	9.4	9.5	0.9
> 30 Microns		0	0	0	0.4	0.9	0.7	1.2	1.2	0
Maximum size	µm	29	29	28	53	50	51	36	41	23
Minimum size		4	5	3	1	1	1	2	1	1
Average Size		13	12	14	10	10	7	13	12	9

QEP (Quantitative Estimation of Phases) (Weight % Normalised to 100)

	RX – D Without Slag	RX– E With 2% ACSS	RX– F with 1% GGBS-SF
C_3S	65.0	66.9	65.9
C_2S	19.1	18.1	19.3
Matrix (C_3A + C_4AF)	21.2	20.6	20.3
Free lime	1.2	0.8	0.9
Periclase	3.5	3.6	3.6

OTHER FEATURES:

- Small Alite size, medium size widely distributed free lime & good aluminate content, may contribute towards adequate early strength potentials.
- The Alite content is good indication of high LSF, well burned nature and well adjusted kiln feed fineness. Alite content slightly more in clinker from RX- E than clinker from RX- D, but slightly lower in clinker from RX- F in comparison with clinker from RX -E
- The average alite size is very small in clinker from raw Mix F compared to clinker from RX- E & D
- Belites are mostly multiple straitioned α' type. Most of belite clusters/nest have voids (pores).The grindability is expected to be good, because of voids & pores. The average belite size is very small in clinker from RX- F compared to clinker from RX- E & D
- The fine to medium grained Matrix is well distributed and porosity of grain is medium to high.
- Periclase is observed as small clusters and randomly scattered, all periclase are very fine , less than 10 micron size. Though MgO is very high, the nature of occurrence of MgO in the clinker as fine periclase crystals(<10 micron) ,indicates low soundness risk with PPC. However OPC may have soundness problem.
- Free lime was present in most grains mostly as small open clusters, most of free lime were more than 200 microns far from belite clusters. Free lime content is decreased in clinker from RX- E & F compared to clinker from RX- D.

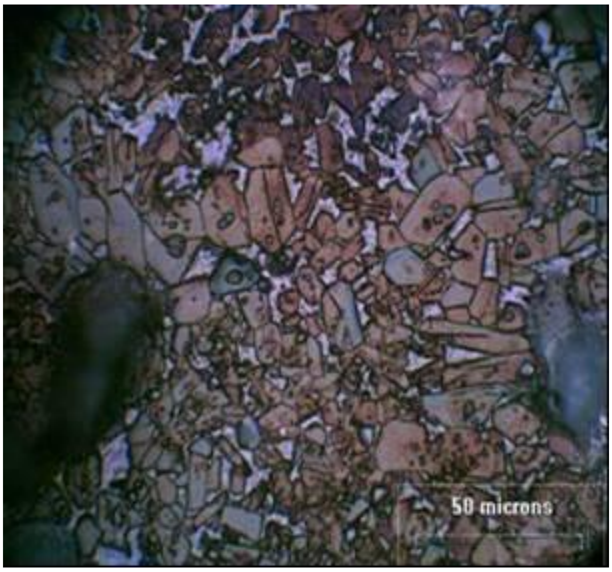


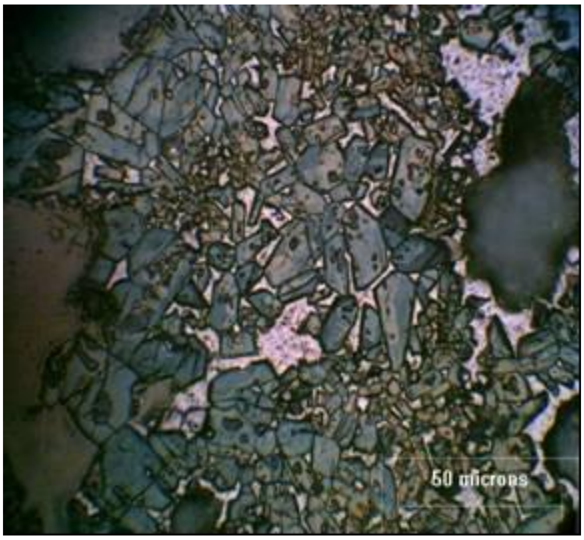
Clinker from RX D Without Slag

Well developed aliite crystals of variable sizes in ferrite/aluminate rich segregated matrix of the clinker grains

Clinker from RX E With 2% ACSS

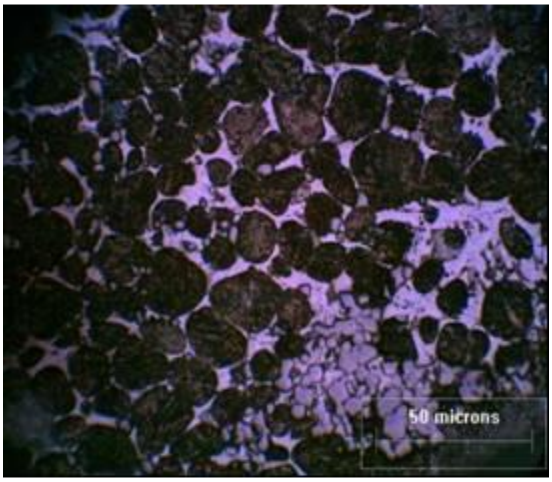
Well developed euhedral alite crystals in a clinker grain indicating well burned raw mix



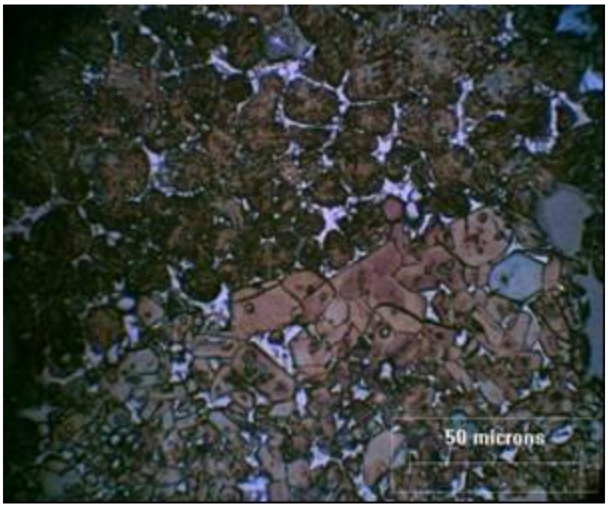


Clinker from RX F With 1% GGBS-SF

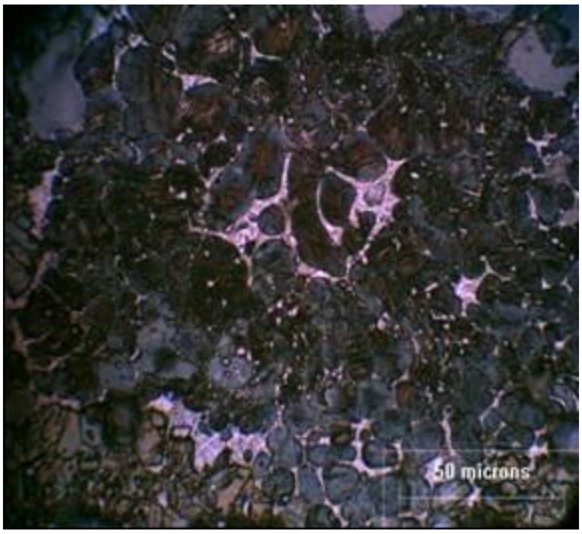
Well developed elongated alite crystals in the aluminate rich matrix



Clinker from RX D Without Slag
Cluster of belites the clinker grains indicating coarse siliceous grain in klinfeed

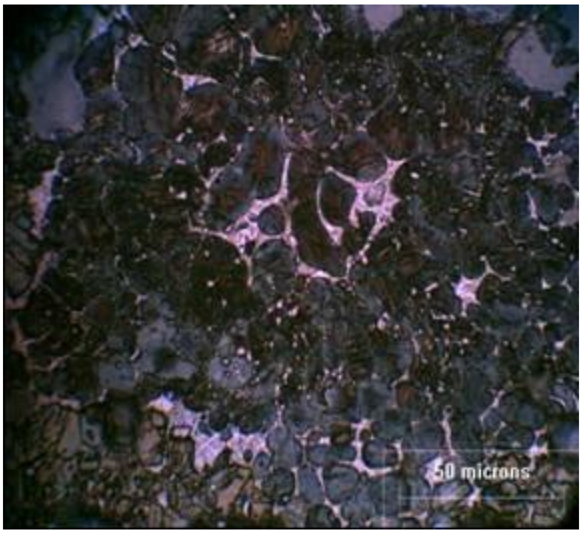


Clinker from RX E With 2% ACSS
Well developed belite cluster crystals of variable sizes along with alites in aluminate rich matrix of the clinker grains



Clinker from RX F With 1% GGBS-SF

Well developed multiple striated belite cluster in aluminate rich matrix of the clinker grains



Clinker from RX D Without Slag

Well developed small free lime cluster along with scattered periclase in the clinker grains

Clinker from RX E With 2% ACSS
Free lime cluster in the clinker grains indicating coarse calcite grain in kiln feed

Clinker from RX F With 1% GGBS-SF
Cluster fine freelime with fine scattered fine periclase crystals grain in the clinker

6.0 Quality of OPC from Pilot Scale clinkers:

Pilot scale clinkers were produced by firing the raw mixes in the pilot scale facility at Q&PD. Laboratory ground OPC were prepared from clinkers, the surface area maintained for OPC was ~320 M^2/Kg & SO_3 content in the OPC was targeted to ~2.4%.

The laboratory ground cements thus obtained were evaluated for physical properties & test results of the same are presented below.

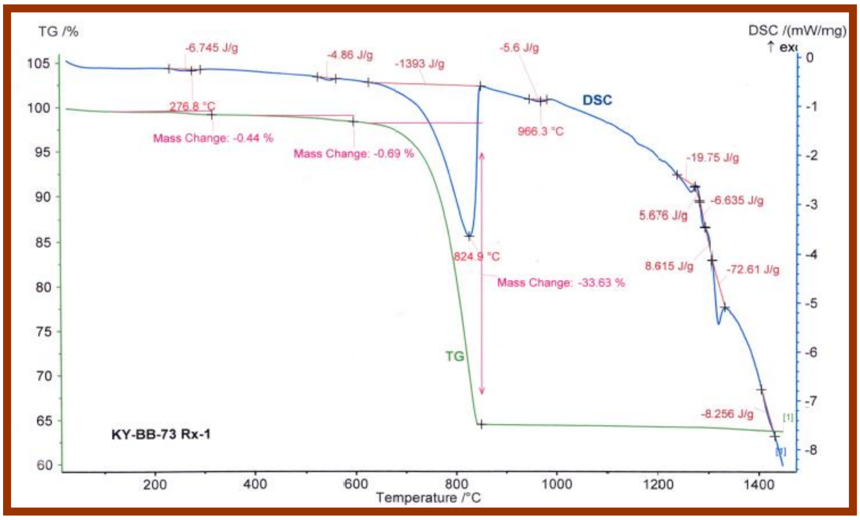
	OPC Prepared From					
	Raw mixes targeting high A/F of ~ 1.65			Raw mixes targeting low A/F of ~ 1.45		
	RX A Without slag	RX B With 2 % ACSS	RX C With 1% GGBS-SF	RX D Without slag	RX E With 2% ACSS	RX F With 1% GGBS-SF
Sp. Surface (m^2/Kg)	**339**	**335**	**331**	**339**	**337**	**327**
N.C (%)	**28.3**	**28.8**	**28.5**	**27.3**	**27.8**	**28.5**
Setting Time (mins)						
Initial	**155**	**150**	**155**	**145**	**165**	**135**
Final	**200**	**210**	**215**	**195**	**220**	**205**
Compressive Strength (MPa)						
1 Day	**16.9**	**17.7**	**18.2**	**16.5**	**18.3**	**18.7**
3 Days	**31.0**	**33.1**	**33.5**	**29.8**	**32.2**	**32.9**
7 Days	**48.0**	**49.6**	**50.2**	**45.3**	**47.3**	**48.3**

The above data indicates following

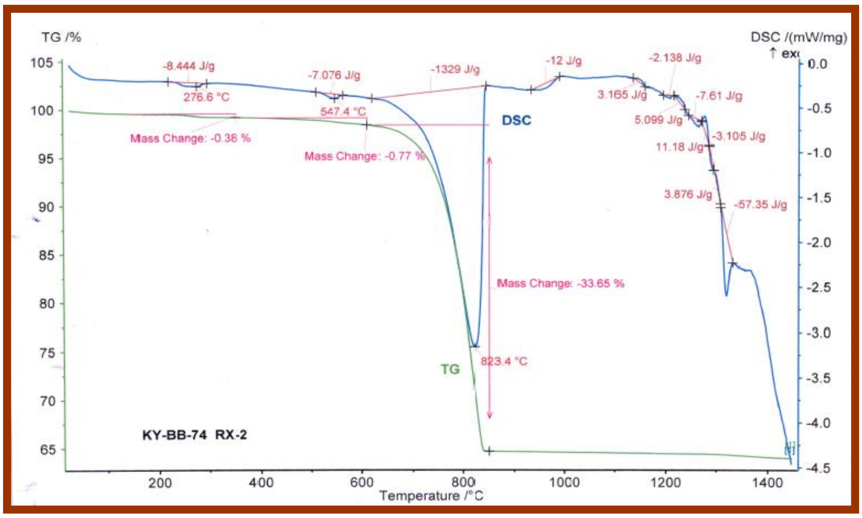
- With use Slags as corrective in Raw Mixes, by an large strength development is better than Raw Mix without Slag
- The Strength development in OPC at 3 Days with use of ACSS & GGBS – SF at A/F of 1.65 are comparatively higher by **~ 1 MPa** than Raw mix with these slags at A/F of 1.45.
- The Strength development in OPC at 7 Days with use of ACSS & GGBS – SF at A/F of 1.65 are comparatively higher by **~ 2 MPa** than Raw mix with these slags at A/F of 1.45.

Annexure

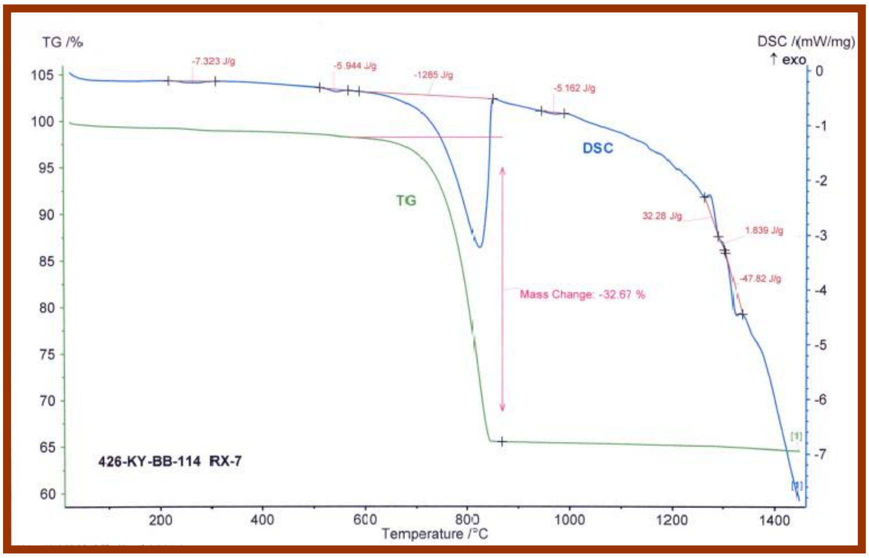
TG /DSC Scans OF Raw Mixes at A/F 1.65



RX –A Without Slag

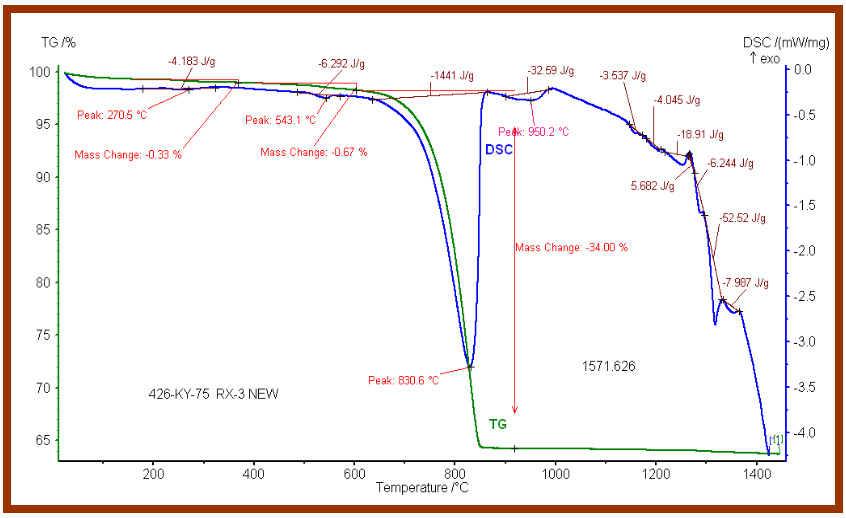


RX –B With2% ACSS

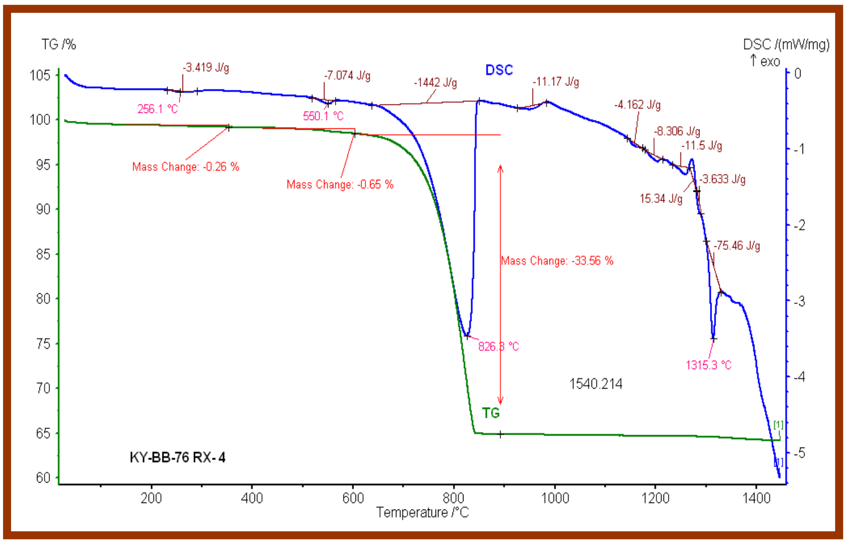


RX –C With1% GGBS-SF

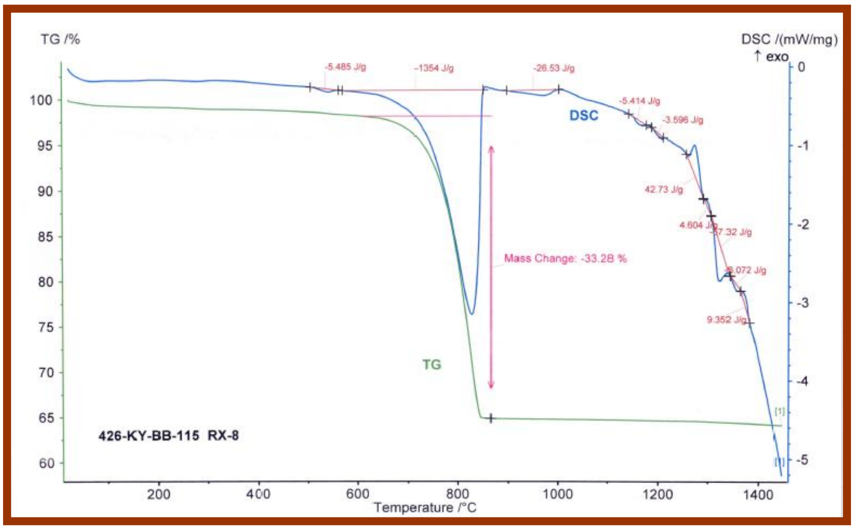
TG /DSC Scans OF Raw Mixes at A/F 1.45



RX –D Without Slag



RX –E With2% ACSS



RX –F With1% GGBS-SF