Fly Ash Utilisation for Value Added Products
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Enhancement of reactivity and increased usage of low lime class-F-fly ash-possible avenues

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ABSTRACT

The low lime class-F fly ash available in the country shows high degree of variability in the quality, higher content of crystallites, lower glassy phase which accounts for lower of usage in cement and concrete. The lime reactivity test used for assessing the pozzolanicity of fly ash did not always correlate with its observed reactivity in Blended cements. An alternative rapid alkali reactivity test developed at the authors' laboratory is illustrated in the paper. The paper also discusses the possibility of increasing the reactivity of fly ash and effect of the reactive fly ash on characteristics of PPC and concrete. The paper further discusses other avenues of fly ash utilisation, which could be categorised as low, medium and high value applications. One of such applications developed at the authors' laboratory that merits special interest, is the Hydrogel process of clinkerisation, which has a potential for utilisation of 20-30% fly ash as a raw material in cement manufacture.

Key words : *Low lime class F-flyash, Fly ash utilisation*

1.0 INTRODUCTION

The fly ash generation in India is about 60 million tonnes annually and considering the developmental programme in the energy sector, it is expected to reach a level of around 100 million tonnes by 2000 AD, which is estimated to require around 28,000 hectares of land for dumping purposes. The existing levels of utilisation of fly ash is only 2-3%, reasons for which are many. However, one of the main reasons is the high degree of quality variation of fly ash.

As a part of an R&D programme on fly ash utilisation, fly ashes from different sources in the country were evaluated for their chemico-mineralogical and pozzolanic characteristics. The paper presents the generated data and infers that the degree of variability in fly ash quality is very high and that there is less correlation between the lime reactivity and cement replacement test values of the fly ashes.

The paper discusses the alkali-reactivity test for fly ash, developed at the authors' laboratory and the attempted correlation between the alkali reactivity values and quality of fly ash culminating into an empirical equation for predicting the desired fineness for a given fly ash so as to have L.R. & C.R. values (reactivity of flyash) conforming to BIS requirements for blended cement.

Researchers world over are looking into the possibility of increasing the reactivity of fly ash for maximising its usage in blended cement and as a cementitious component in concrete, without affecting the quality of the final product. Various alternatives reported in literature and some of which are being studied at the authors' laboratory include :

* Use of Physical/Chemical processing of fly ashes
* Controlling the quality of flyash at the stage of its generation could be an attractive alternative, however attempts on this aspects are practically not reported in literature.

The authors have discussed the reported / available data indicating the improved quality of the blended cement / concrete with use of the reactive flyash.

Besides the conventional applications of flyash such as (a) manufacture of bricks, (b) as pozzolana in blende cement (c) in mass concreting, etc. other reported applications of fly ash briefly touched upon by the authors can be categorised into low, medium and high value applications, wherein fly ash can be used either as a raw material or as a resource material for the value added products.

One of such applications developed at the authors' laboratory that merits special interest, is the Hydrogel process of clinkerisation, in which flyash is activated with alkali. Using activated fly ash, a hydrogel can be prepared which on sintering produces cement clinker. This new process route has a potential of using fairly high levels of fly ash.

2.0 FLY ASH CHARACTERISATION

2.1 Characterisation of fly ash from different sources

Fly ash samples form different coal fired thermal plants in the country were evaluated for their physico - chemical characteristics. The data is summarised in Table-1. The data indicates that the fly ash available in the country is a low lime Class-F Fly ash. The variation in fineness, lime reactivity and cement replacement test values for the fly ashes is graphically represented in Fig. 1.

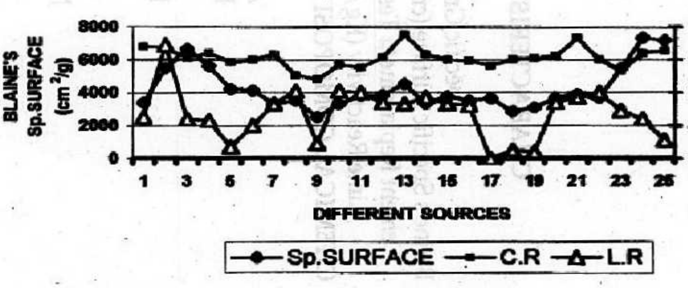


Fig. 1 : Variation of blaine's fineness, C.R. & L.R. of Fly ash of different sources

Table - 1 : Physico-chemical characteristics of fly ash of different sources

CHARACTERISTICS	1	2	3	4	5	6	7	8	9	10	11	12
Specific Gravity	2.35	2.31	2.39	2.32	2.52	2.17	2.17	2.30	2.38	2.15	2.28	2.43
Blaine's Specific Surface (cm^2/g)	3400	5475	6670	5620	4200	4130	3340	3500	3250	3305	3825	3850
Cement Replacement Test (%)	88	87	81	84	78	80	83	71	68	77	75	81
Lime Reactivity (Kg/cm_2)	45	89	44	43	27	40	53	61	29	61	60	54
CHEMICAL COMPOSITION												
SiO_2	55.5	55.9	55.8	57.0	50.1	60.7	59.8	56.4	54.1	54.7	56.0	53.0
Al_2O_3	28.9	32.3	33.0	31.9	25.8	29.0	26.4	25.2	21.9	31.1	30.8	26.0
Fe_2O_3	4.1	5.5	4.3	4.2	9.7	4.3	7.0	6.4	6.2	3.6	4.0	5.2
CaO	1.8	1.7	1.9	2.0	3.7	1.2	1.7	1.9	1.9	0.6	0.6	0.8
MgO	0.6	1.1	1.0	1.0	0.8	0.9	1.1	1.1	1.1	0.2	0.2	0.2
LOI	5.5	0.4	0.8	0.7	7.8	0.7	0.9	5.4	11.7	6.9	5.7	12.2
SO_3	0.1	0.1	0.3	0.3	1.0	0.1	0.1	0.1	0.1	0.2	0.2	0.2
Na_2O	0.01	0.07	0.11	0.12	0.29	0.08	0.07	0.09	0.09	0.15	0.11	0.08
K_2O	1.55	0.72	0.96	0.94	0.84	1.00	1.22	1.87	1.70	1.40	1.21	1.16

CHARACTERISTICS	13	14	15	16	17	18	19	20	21	22	23	24
Specific Gravity	2.16	2.55	2.23	2.34	1.95	2.32	2.35	3.04	2.63	2.28	2.27	2.8
Blaine's Specific Surface (cm^2/g)	4530	3325	3765	3500	3655	3225	3085	3670	3910	3675	5460	7300
Cement Replacement Test (%)	95	83	80	79	76	80	81	82	93	80	73	
Lime Reactivity (Kg/cm^2)	53	57	53	52	20	25	24	54	57	60	49	44
CHEMICAL COMOPOSITION												
SiO_2	59.7	58.0	58.1	61.1	60.0	59.8	59.1	55.4	62.0	60.8		65.4
Al_2O_3	25.5	28.2	23.6	22.3	21.9	29.1	30.4	28.8	26.8	21.0		19.5
Fe_2O_3	3.7	4.4	5.1	6.1	8.8	4.3	4.1	3.2	6.1	6.8		4.1
CaO	1.0	3.4	3.4	0.8	0.9	0.7	0.6	1.0	1.2	3.2		0.6
MgO	0.7	0.4	0.6	0.8	0.6	0.8	1.0	1.2	0.8	1.5		0.1
LOI	5.9	3.3	5.9	5.5	6.5	1.7	1.1	7.2	0.8	4.2		4.2
SO_3	0.1	0.1	1.0	0.2	0.1	0.1	0.1	0.1	0.2	0.1		0.3
Na_2O	O.13	0.05	0.18	0.12	0.11	0.06	0.05	0.07	0.07	-	-	-
K_2O	1.65	0.77	0.74	1.05	1.00	1.32	1.25	0.90	0.64	-	-	-

2.2 Variability of fly ash from same source

The quality of fly ash from the same source also shows a high degree of variation depending on operating conditions of the thermal plant, efficiency and type of ESP fields, Fig.2 illustrates the variation in fineness and Table 2 depicts the reactivity of the composite fly ash from different ESP fields of the different units of the same thermal plant. The effect of the variation in quality of flyash on the quality of Portland Pozzolana Cement is shown in Fig. 3.

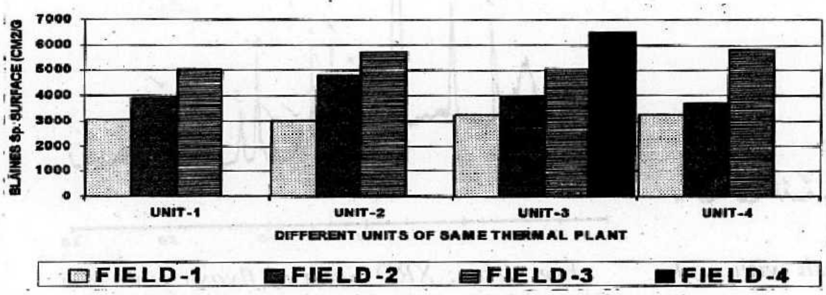


Fig. 2 : Variation in blaines specific surface of different ESP fields of different units and at same location

Table 2 : Characteristics of fly ash of different ESP-fields from the same units

Characteristics	*Fly Ash-1*	*Fly Ash-2*
specific surface (Cm^2/g)	3225	4850
Lime reactivity (Kg/cm^2)	25.0	45.0
cement replacement test value (%)	80.0	84.0

ppc - 1: prepared with 20% fly ash-1

ppc - 2: prepared with 20% fly ash-2

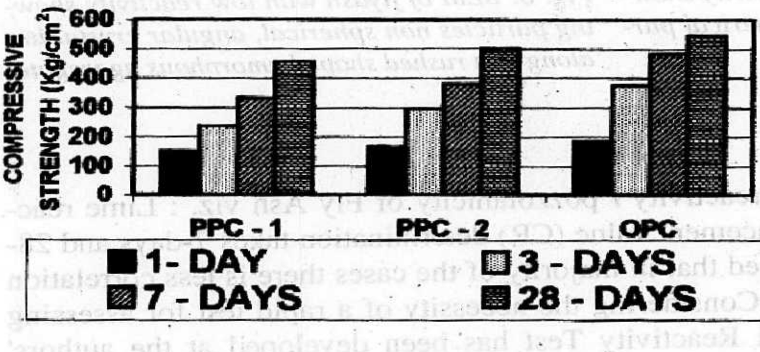


Fig. 3 : Quality of PPC with Flyash of different ESP fields

2.3 Mineralogy and morphology of fly ashes of high and low reactivity

Mineralogical, microstructural, and morphological Studies on Fly ash samples indicate that less reactive fly ashes have relatively lower amorphous phase and higher crystallites with higher content of angular particles. Fig. 4 a&b indicate the mineralogical difference between the fly ash with high reactivity and with low reactivity. The morphological characteristics of these fly ashes are depicted in Fig. 5 & 6.

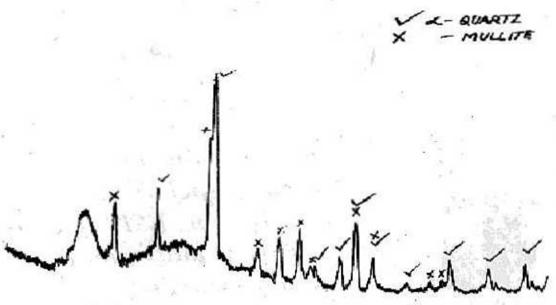


Fig. 4(a) : XRD Scan of flyash with high reactivity

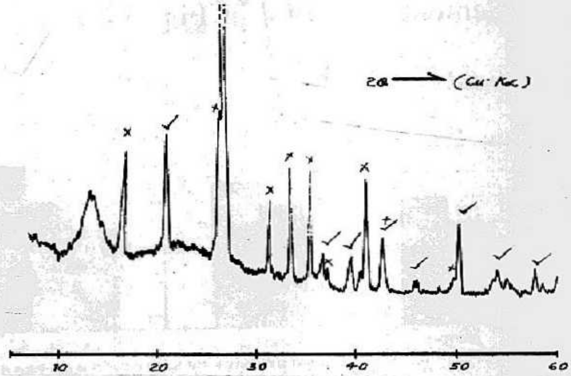


Fig. 4(b) : XRD Scan of flyash with low reactivity

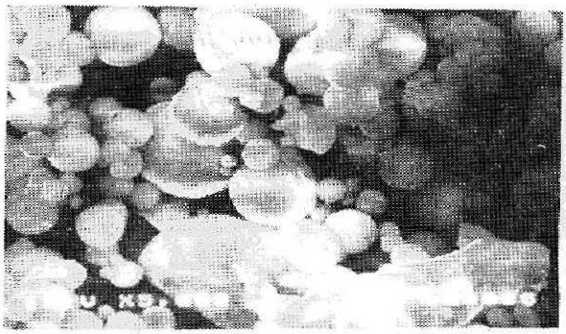


Fig. 5 : SEM of flyash with high reactivity showing high glassy, smooth surfaces spherical particles

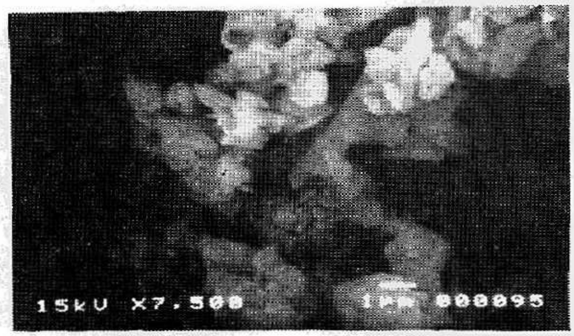


Fig. 6: SEM of flyash with low reactivity showing particles non spherical, angular crystallites alongwith rushed shaped amorphous aggregates

2.4 Alkali reactivity test

The tests used for assessing the reactivity / pozzolanicity of Fly Ash viz. : Lime reactivity Test (LR) and cement replacement value (CR) determination takes 7-days and 28-days respectively and it is observed that in majority of the cases there is less correlation between the LR and CR values. Considering the necessity of a rapid test for assessing the quality of flyash, the Alkali Reactivity Test has been developed at the authors' laboratory[1]. Using the Alkali reactivity value (R_A), an attempt was made to evolve the inter-relationship between the fly ash characteristics, viz. Alkali reactivity value (R_A), Lime Reactivity (LR), Cement Replacement Test Value CR) and the fineness (Blaine's specific surface).

The statistical analysis indicate a strong relationship between the fly ash characteristics as indicated by the correlation coefficient of 0.88. The correlation could be represented by an empirical equation given below:

Blaine's specific Surface (cm^2/g)= -3136 - 0.236 R_A+44.84 L.R+63.63.76C.R.

Table-3 : Fly ash characteristics of some fly ash samples along with the predicted values of Blaine's Specific surface

Alkali Reactivity value (R_A)	L.R.	C.R.	Blaines sepcific surface (cm^2/g)	
			Observed	Predicted
150	39	73	3300	3723
250	71	86	5380	3700
200	25	80.2	3135	3711
195	27	78	3300	3712
332	65	88	5200	3680
135	61	82	4800	3726
310	63	83	4440	3685
300	57	93	4800	3687
280	51	78	4400	3692
210	40	75	3483	3708
310	89	96	8080	3685
310	90	84	6180	3685
315	24	79	3180	3683
290	24	84	3200	3690
230	43	80	4200	3704
250	25	84	3025	3699
380	40	80	3680	3668
270	53	80	3765	3694
250	46	74	3615	3700
180	44	84	4200	3715
230	70	85	4500	3704
170	41	72	3400	3718

**Predicted Values of Blaine's Specific Surface as Calculated from the Empirical Equation to Achieve L.R Value of (40Kg/cm^2) & C.R. Value of 80%*

This equation could be used to assess the optimum fineness to which a given fly ash should be ground to achieve the LR(>40) and CR>80) values well above the requirements of BIS. The Table-3 gives the characteristics of a set of fly ash samples along with the predicted values of fineness. These studies indicated that the reactivity of the finer fractions of fly ash is higher than the coarser fractions can be substantially increased by finer grinding.

2.5 Enhancement of reactivity of fly ash

The avenues being looked into by researchers for enhancing the reactivity of fly ash, thus maximising flyash incorporation in PPC and improving the quality of the flyasn based concrete are:

(a) Air classification: As discussed earlier the finer fraction of the flyash (i.e below 45μ) has higher pozzolanicity / reactivity. The technical feasibility of using specially designed mechanical air separators for the Indian fly ashes has been examined and recommended by D.S. Venkatesh et al [2]. The compressive strength characteristics of the PPC with 15 & 30% flyash of different fineness as reported by Berry et al[3] is illustrated in Fig. 5.

(b) Grinding of Fly ash below 45 microns also exhibits substantial improvement in the quality of the resultant PPC. At 20% incorporation levels of the ground Flyash the setting time and early compressive strengths are comparable to the OPC. (Fig. 6)

(c) Chemically, the reactivity of fly ash can be substantially enhanced by revitrification of fly ash mixed with varying concentration of soda ash, red mud or iron at 1300-1500°C and rapidly quenching the sintered product. The chemical processing resulted in substantial improvement of lime reactivity to the tune of 60 to 100 kg/cm^2 due to higher vitrification and silica solubility[4].

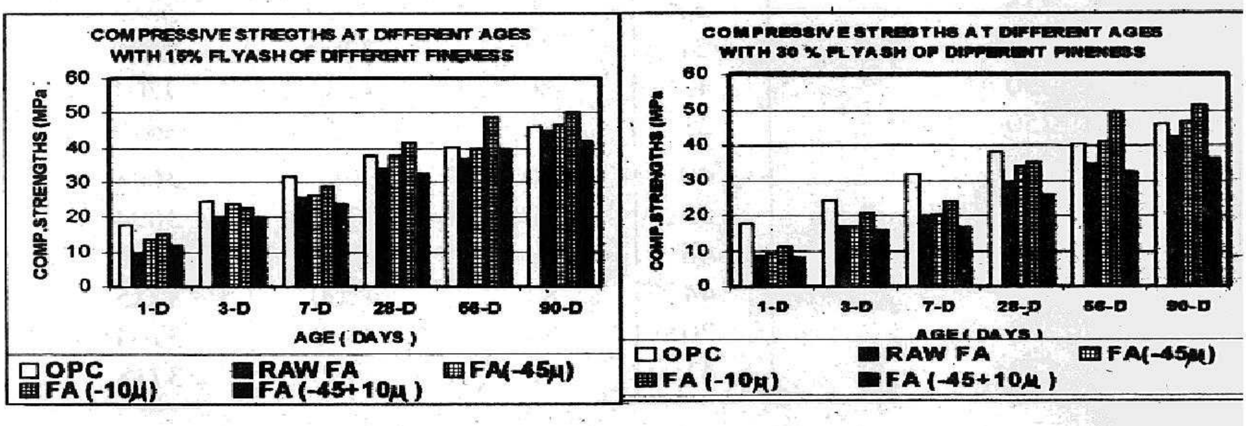
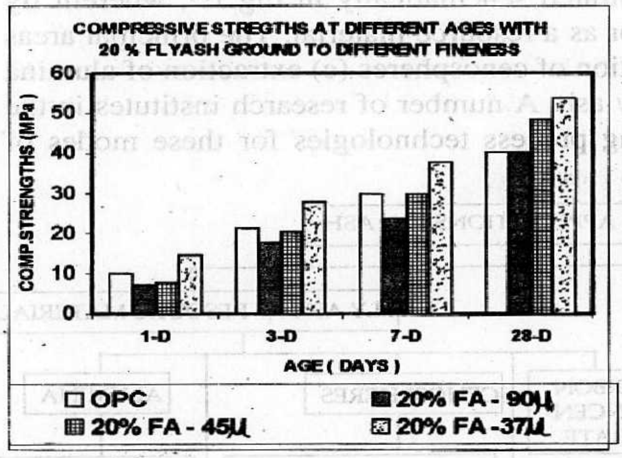


Fig. 7 : Quality of PPC with 15% & 30% classified Fly ash of diffeent fineness



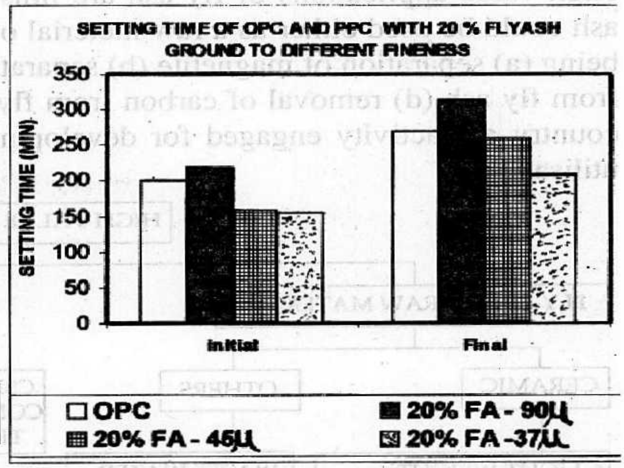


Fig. 8 : Quality of PPC with fly ash ground to diffeent fineness

3.0 AVENUES FOR UTILISATION

Avenues for flyash utilisation can be categorised into low, medium and high value applications, wherein fly ash can be used either as a raw material or as a resource material for the value added products. The low and medium value applications are summarised in Table-4[5], most of which are on a growing trend in the country.

Table-4 : Low and medium ppplications of fly ash

LOW VALUE	MEDIUM VALUE
* Mine fills / Embankments	* Portland cement clinker
* Use in road construction	* Portland pozzolana cement
* Lime - fly ash stabilized soil	* Masonry cement
* Lime - Fly ash concrete	* Oil well cement
* Lean - cement - fly ash concrete	* Fly ash building bricks
* Lime-fly ash bound macadam	* Fly ash blocks
* Cement fly ash concrete	* Pre-cast fly ash building units
* Partial replacement of cement in Mortars and mass concrete	* Lime-fly ash cellular concrete
* Reinforced fly ash cement concrete	* Cement fly ash concrete and Ready mixed fly ash Concrete
* Fly ash in grouting	* Sintered fly ash light weight aggregate and concrete
	* Aerated concrete

High value applications of fly ash are illustrated schematically in Fig.7[6], wherein fly ash could be used either as a raw meterial or as a resource material. The principal areas being (a) separation of magnetite (b) separation of cenospheres (c) extraction of alumina from fly ash (d) removal of carbon from fly ash. A number of research institutes in the country are activity engaged for developing process technologies for these modes of utilisation.

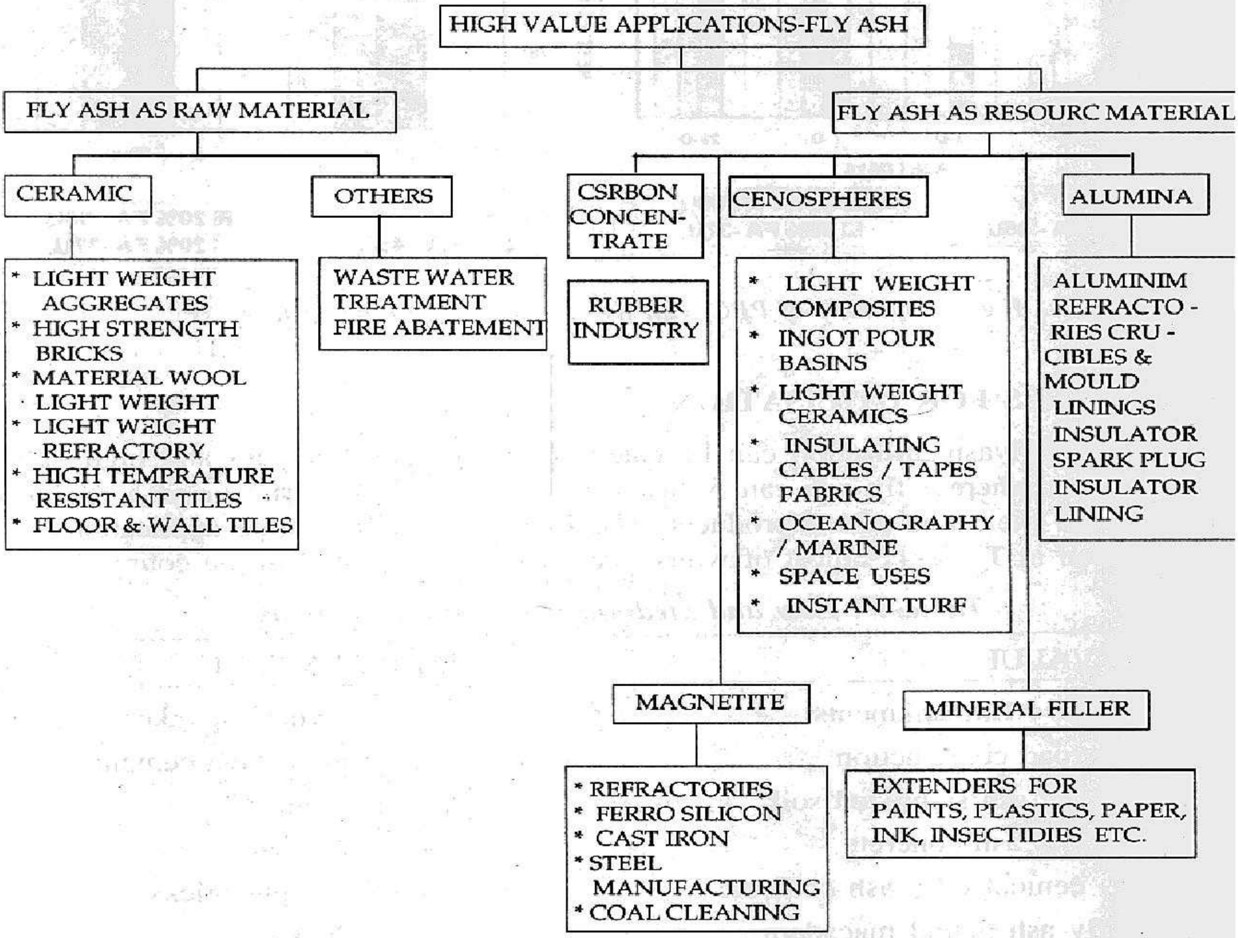


Fig. 9 : Fly ash Utilisation for high value added products

One of such specialised applications developed at the authors' laboratory which has a high potential for fly ash utilisation is the hydrogel process[7]

The process involves activation of fly ash with alkali. The activated fly ash is reacted with hydrated lime which is composed of calcium-Silicate-Aluminate-Hydrate(C-S-A-H) and calcium silicate Hydrate (C-S-H) precursers. The prcipitated gel on de-watering followed by sintering produces the cement clinker. The critical steps in the hydrogel process of clinkerisation is illustrated in Fig. 8. The process utilises fly ash to the tune of 25-30% ,and the clinkerisation temperature required are 1100-1350^{0}C depending on the Phase composition of the clinker targeted. The raw material proportions and clinker composition along with the quality of the resultant cement are shown in Table 5.

Table 5 : Raw material proportions of the hydrogel mix, chemical composition of clinkers and physical properties of Cements

Raw Material proportions	Hydro-gel Belite-rich mix	Hydrogel Low-belite mix
Activated fly ash	23.5	22.0
Hydrateed lime	76.5	78.0
% Oxides	Cliker-II	Clinker-II
SiO_2	23.36	22.27
AL_2O_3	9.05	8.64
Fe_2O_3	2.74	2.69
CaO	62.51	64.14
MgO	0.23	0.23
Na_2O	0.83	0.8
LSF	0.80	0.86
SA	1.98	1.96
AM	3.3	3.2
Potential phase composition		
C_3s	8.1	25.8
C_2S	60.9	44.4
C_3A	19.4	18.4
C_4AF	8.3	8.2
C/S ratio	2.68	2.88

Physical tests	Cement from Clinker I	Cement from Clinker II
Blaine's Specific surface (cm^2/gm)	3200	3200
SO_3%	2.7	2.7
Consistency (%)	28.3	27.5
Setting (min)		
Initial	75	65
Final	115	105
Comp. strengths (MPa)		
1 Day	13.0	16.5
3 Days	20.0	27.5
7 Days	25.0	36.0
28 Days	38.0	46.0

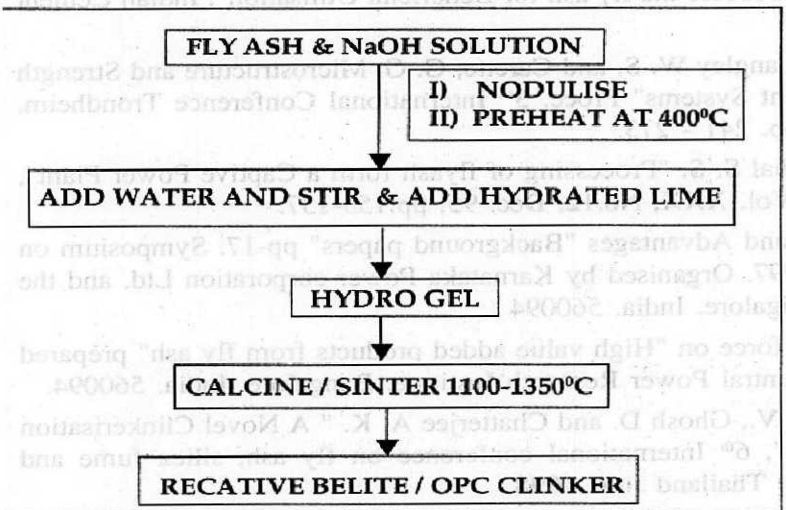


Fig. 10 : Hydrogel Process

4.0 CONCLUSIONS

* The paper illustrates high degree of variation in characteristics through evaluation of fly ash from different Thermal Plants in the country, indicating that the variation in reactivity is primarily attributed to difference in mineralogy and microstructural characteristics of fly ash.
* The observed variability in fly ash quality necessitates a rapid test to assess the suitability of fly ash for PPC. The alkali reactivity test and the empirical equation developed at the authors' laboratory, could be useful for assessing the reactivity/ Pozzolanicity of fly ash and for optimising the fineness of fly ash to achieve maximum pozzolanic properties.
* The reactivity of fly ash can be substantially enhanced by selectively classifying the reactive finer fractions or by grinding the composite fly ash finer (size fraction passing 45-37 microns)
* The paper summarises the reported avenues of flyash utilisation categorising them in to low, medium and high value applications.
* The paper further discusses the Hydrogel process for clinkerisation developed at the authors' laboratory indicating that the process has a good potential for fly ash utilisation, the economics of the process is currently under examination.

5.0 REFERENCES

1. Kulkarni P. C., Kaduskar P. S., Khadilkar S. A. and Cursetji R. M. "Chemical-Mineralogical characteristics and assessment of reactivity of fly ashes of different sources", National Seminar on Performance enhancement of cements and concretes by use of Fly ash, Slag, Silica fume and chemical admixtures, New Delhi, Jan. 1998, II - 91.
2. Venkatesh D. S., Harish D. V. "Process the fly ash for Beneficial Utilisation", Indian Cement Review Dec. 1997, pp.25-28.
3. Berry E. E., Hemmings R. T., Langley W. S. and Carette; G. G. Microstructure and Strength development in Portland Cement Systems" Proce. 3rd International Conference Trondheim, Norway, 1989, SP-114 Vol.1 pp. 241 - 273.
4. Garg S. K., Lal Kishen and Rehal S. S. "Processing of flyash form a Captive Power Plant", Chemical Engineering World, Vol. XXX, No.12, Dec. 95, pp.155-157.
5. Pai. B.V.B. "Fly Ash; Its uses and Advantages "Background papers" pp-17. Symposium on Fly Ash Utilisation-10th Jan. 1997. Organised by Karnataka Power corporation Ltd. and the associated cement cos Ltd. Bangalore. India. 560094
6. Detailed Project Report of task force on "High value added products from fly ash" prepared by fly ash Utilisation Group, central Power Research Institute. Bangalore. India. 560094.
7. Khadilkar S. A., Karandikar M. V., Ghosh D. and Chatterjee A. K. " A Novel Clinkerisation Process for Fly-Ash utilisation", 6th International conference on fly ash, silica fume and Natural Pozzolanas in Concrete, Thailand June 1998.