3rd International Conference

FLY ASH

UTILISATION & DISPOSAL

19 - 21 February 2003
New Delhi, India

PROCEEDINGS

Vol - I

Editors

G.N. Mathur **Kuldip Singh**
Vimal Kumar **R. Krishnamurthy**

CENTRAL BOARD OF IRRIGATION AND POWER
Malcha Marg, Chanakyapuri, New Delhi-110021
Tel.: 91-11-26115984, 26876229 Fax 91-11-26116347
E-Mail : cbip@cbip.org ; info@cbip.org ; cbip@vsnl.com
Web : www.cbip.org

FUTURE TECHNOLOGICAL OPTIONS FOR INCREASED FLY ASH UTILISATION– A REVIEW

S.A.Khadilkar,

SYNOPSIS:
Nearly 73% of India's total installed power generation capacity is thermal, of which coal-based generation is 90%. Presently 90 million tonnes of fly ash is being generated annually in India, with 65 000 acres of land being occupied by ash ponds. The use of coal of high ash content (30%–50%) contributes to these large volumes of fly ash. By end of 11th five year plan the fly ash generation in the country is estimated to reach 110-120 million TPA. India's dependence on coal as a source of energy remains unchanged. Thus, it is but natural that fly ash management in the country would be important and of national concern.

Such huge quantities of generation would pose challenging problems, in the form of land usage, health hazards, and environmental dangers. Both in disposal, as well as in utilization of fly ash , utmost care would have to be taken, to safeguard ecological balance of the surroundings.

The percentage fly ash utilisation in the country has registered a significant increase from 3 - 5% in late eighties and early nineties to the present levels of around 13% utilisation . However this growth trend is too minimal considering the total quantities of generation. It should be of knowledge here that there are countries, which have reached levels of 80 – 100 % fly ash utilisation levels.
A recent survey carried out on spatial distribution of the thermal plants in the country indicates that these locations could be broadly classified into four categories:

- Plants located in major/metro cities and their periphery
- Plants located near coal pitheads.
- Plants located near consumer industries (Cement plants).
- Plants not located under the above categories.

Thus depending on the locations of the generation sites , suitable technological options need to be selected and evolved for enhancing the levels of fly ash utilisation of the country.

In case of thermal plants located near cement plants and near major/metro cities, the main avenue for utilisation of fly ash would be its maximized usage in Cement & concrete . In the tropical climatic conditions of India , the fly ash based products are being accepted as the most effective option for durability and performance . This awareness would help increase its utilisation in these areas of applications.

This paper initially discusses briefly the quality characteristics of the low lime Class – F fly ashes available in the country and illustrates that they are in no way inferior to their European counter parts (low lime Class - F fly ash), in their pozzolanic activity in blended cements and in their use as inorganic admixtures , in concrete as illustrated by the studies carried out at the authors laboratory.

For furthering the utilisation levels of fly ash in cement & Concrete, some of the newer technological options are discussed in the paper in some details. These options include, Processes for improving the pozzolanic activity of fly ash by processing, Processes for decreasing the combustible contents in fly ash, Ash modified clinker technology (AMC technology) a patented process developed in China - which produces a fly ash having cement clinker minerals, Manufacture of Sulpho-aluminate belite cements ,high strength cementitious grouts, cementitious binder and aggregates in pavement applications etc.

The authors opine that in future, the most common feature in cement plants would be Captive power plants using high ash coals , that would generate fly ash , which could be a value added option with use of some of the above technologies.

In the case thermal plants located at distance from the consumer industries, besides the presently used technologies for use of fly ash in fly ash bricks, landfill , soil conditioning etc , there could be other avenues of utilisation which could be looked into, such as fly ash as a source material for alumina with Portland Cement as by – product ,In the manufacture of Zeolites – a raw material for detergent industry , Production of alum from fly ash , for manufacture of artificial soil by SLASH process - which uses sewage sludge , lime and fly ash – partial use of the SLASH also improves the crop yield etc . These technological options could be site specific for maximizing the generated fly ash.

Finally the authors summarize that better acceptance of the fly ash generated in country as a pozzolanic material, selection of an appropriate technology relevant in Indian context and to location of the generation would certainly help increase the levels of its Utilisation.

Introduction:

The need for power has increased manifold mainly due to increased population and rapid industrial growth,. Nearly 73% of India's total installed power generation capacity is thermal, of which 90% is coal-based generation, with diesel, wind, gas, and steam making up the rest. The Thermal power generation through coal combustion produces minute particles of ash which carry over with the flue gases and to prevent their escape to the atmosphere the ash particles are collected in a series of electrostatic precipitators fields. This collected ash is known as fly ash, which is ~80% of the total ash generated in a thermal power station, the balance ~20% is collected at the bottom of the boiler and is known as bottom ash. The fly ash along with the bottom ash is carried to lagoon storage along with water, this ponded fly ash is termed as Pond ash. This wet mode of disposal of the fly ash poses problems in the form of land use, health hazards, and environmental dangers. Both in the disposal and in utilization of the fly ash utmost care has to be taken to safeguard the interest of human life, wild life, and such other considerations of maintaining the ecological balance .

Although the utilisation of fly ash in the country has shown an increase from 5 to 13%, considering the quantum of generation this utilisation levels are minimal.

Various options of furthering the increased usage of fly ash are being pursued in the country by various government and semi government bodies which is resulting in a gradual increase in awareness and acceptance levels of the fly ash based products which is resulting in a gradual increase in the fly ash utilisation levels.

In this paper the authors discuss some of the futuristic technological options reported in literature and experimented on pilot / semi – industrial scales of operation, which could help achieve this objective of fly ash utilisation in a sustainable and substantial way. The choice of the appropriate technology could be a function of the spatial location of the thermal plants viz:

- Plants located near consumer industries
- Plants located in major metros cities and their periphery
- Plants located near coal pit heads
- Plants not located under the above categories

Table-1 shows the Spatial distribution of coal fired power plants [(1)]

Table-1

	Capacity (MW)	**Coal consumption(Mt)**	**Estimated ash generation (Mt)**	**Possibility of utilisation(Mt)**
Large cities	20000	78	31	28
Pit heads	13000	51	20	12
Others	13000	53	21	2
Cement clusters	10000	40	16	10
Total	-	-	**88**	**52**

Note :There is an element of overlap in all categories listed above

Fly ash Characteristics available in the country:

The fly ash available from the coal fired thermal plants in country are fairly uniform in their chemico-mineralogical characteristics . Compositionally they could be classified as Low Lime Class – F fly ash , mineralogically composed of 15 - 30% mullite 15-45 % quatz,1-5% Magnetite, 1-5% Hematite and around 25 - 35% of amorphous glassy aluminao silicate phase [(2)]. The mineralogical composition being governed by coal pulverising system used , bolier type & efficiency , fly ash collection system etc .

The quality of fly ashes from different Thermal plants /different ESP fields in terms of the prevalent tests - Lime Reactivity (LR) and Cement replacement Value test (CR) and fineness in terms of Blaines sp. Surface is graphically shown in Fig. 1. Assessment of the quality of fly ash through Lime Reactivity (LR) and Cement replacement test (CR) really does not give a insight into the reactivity of fly ash , at the authors laboratory Alkali reactivity test has observed to indicate the reactivity of fly ash in terms of its R_A – Alkali reactivity value , the test is a rapid test for assessment of the fly ash reactivity , details of which have discussed in one of the publications [(3)] . This test could be used to optimize the grinding fineness of fly ash to derive its maximum pozzolanic potential. The Table-2 illustrates the physico chemical characteristics of fly ash from different sources in the country.

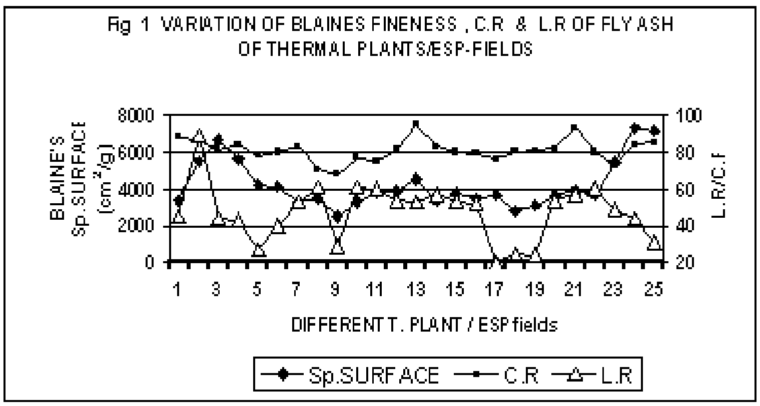

Table-2: Physico-Chemical Characteristics of Fly Ash of Different Thermal plants/ESP fields

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 COMPOSITION												
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	0.13	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	-	-	-

Pozzolanic Reactivity of Indian Fly ashes:

The shift in the emphasis of construction industry from high strength to high performance concrete , has resulted in increased acceptability of fly ash based blended cements in India. Irrespective of the arguments on the necessity of strength gradation for blended cements, it is the requirements of the present market scenario to have the product at comparative levels of quality to OPC, with maximised levels of the pozzolanic component in order to provide the product with added merits of lower heat of hydration, lower permeability, improved durability, through higher sulphate resistance, corrosion resistance and resistance to ASR expansion thus resulting in an improved performance of the resultant concrete . The USP's of these fly ash blended cements can be primarily attributed to decreased availability of calcium hydroxide in hydrated cement paste due to secondary pozzolanic reactions with fly ash and the low lime class – F fly ashes available in the country are compositionally most suited in terms of durability of the resultant concrete . The pozzolanic reactivity of the Low Lime Class – F fly ashes available in the country has been observed to be more a function of glassy amorphous content and the particle characteristics, it is independent of the minor variations in the chemical compositions . On an average the amorphous content of Indian fly ash is in the range of 25 - 35%, where as comparatively compositionally similar Class – F, European fly ashes have relatively higher amorphous phase contents (40 -70%). At the authors laboratory comparative hydration studies carried out to assess the relation between the amorphous glassy phase contents and the reactivity of low lime fly ashes [(4)] indicates that the percentage reaction of the fly ash of different amorphous phase contents at different ages of hydration appear to be nearly similar except for the difference in the initial rate of hydration and the type of the different types of hydrates formed during the hydration of fly ash based blended cements made with fly ashes of low (Fly Ash-In) , medium (Fly ash – U) and higher (Fly ash – A) amorphous glassy phase contents . The Fig.2 indicates the free calcium hydroxide content of the hydrated cement pastes (PPCs) , at different ages of hydration and Fig: 3 illustrates the % reaction of the fly ash component in the different PPCs at the tested ages of hydration

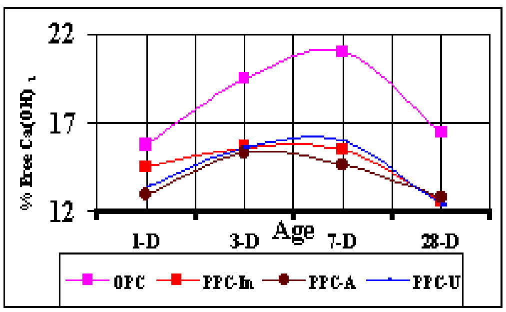

Fig. 2: Free Calcium Hydroxide in hydrated Cements at different age of hydration

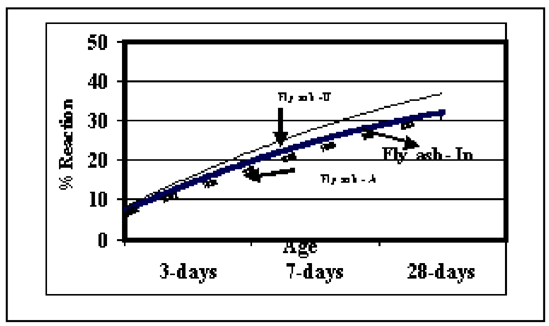

Fig: 3 : % Reaction of the fly ash in different PPC s

The studies indicate that after a certain minimum value of the amorphous glassy phase contents , the reactivity of the fly ash appears to be independent of further increase in the glassy contents . Thus the particle characteristics of the fly ash plays a dominant role in the influencing the properties of the resultant PPC and concrete as this property would govern the particulate plasticising effect, as also the packing effect.

Future Technological Options for enhancing fly ash Utilisation:

Some of the common reported applications of the fly ash in low, medium and high value products is summarized below in Table-3&4

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 , Fly ash Blocks , Sintered Fly ash light weight aggregate
• Lime –Fly ash bound Macadam	• Pre- cast Fly ash building units
• Cement Fly ash Concrete	• Lime –Fly ash Cellular Concrete
• Fly ash in grouting	• Ready mixed Fly ash Concrete & Aerated Concrete

Table 3 – Low and Medium value applications of Fly Ash

Fly ash as Raw material	Fly ash as Resource material
• Ceramics	• Carbon Concentrate
• Waste water treatment	• Cenospheres
• Fire Abatment	• Alumina
• Lightweight aggregate	• Magnetite
• High strength bricks	• Mineral Filler
• High temperature resistance tiles	
• Floor & wall tiles	

Table- 4 : High value applications of fly ash

Technologies for enhancing the pozzolanic reactivity of Fly ash :

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

Air classification: The finer fractions of the flyash (i.e below 45 μ) have 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 [(5)]. The compressive strength characteristics of the PPC with 30 % fly ash of different fineness as reported by Berry et al [(6)] is illustrated in Fig. 4 .

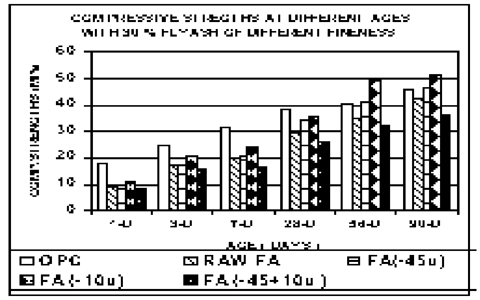

Fig.4 Comp. Strengths of cements with 30% Fly ash of different size fractions

Separation Technique :

Based on the fly ash characterization results, a separation process has been developed by Hwang et al [(7)] to yield high quality fly ash materials and to develop utilization technologies so that new applications and markets for fly ash can be generated .The separation process consists of a gravitational separation process to separate the cenospheres , a magnetic separation process to separate the iron oxide spheres, and a froth flotation process to separate the unburned carbon[(8,9)]. The material left after these separations is designated as clean ash, which is a good pozzolanic material.

The separation technique is illustrated in Fig 5

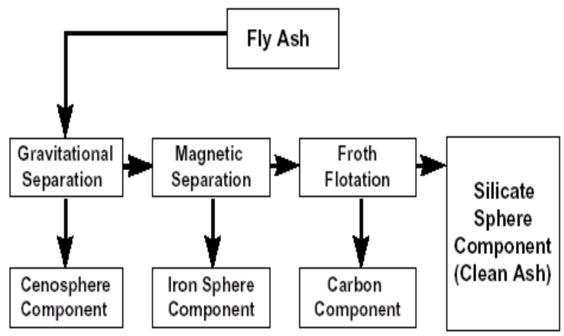

Fig.5: Fly ash Separation Process

Mechanical activation:

Mechanical activation essentially involves grinding of fly ash , which results into three major changes in physical characteristics of fly ash, an increase in its fineness, an increase in bulk density and changes in shape of the particles . In certain fly ashes with very small size of spherical particles the destruction of these particles is negligible.

Mechanical activation of fly ash has been the topic of interest amongst the scientist worldwide, Matsufuji et al [(10)] studied the properties of Concrete with Ultra-Fine Particles Produced from Fly ash by mechanical activation ,while Ziyi [(11)], carried out research on superfine fly ash and its activity in cement, Paya et al [(12,13,)] evaluated the effect of mechanical treatment on physico-chemical characteristics of fly ash and its effect in cement mortars. Monzoet al [(14)] evaluated the granulomteric influence of ground fly ash on mortar strength.

Table- 5: Density and strength of Mortar prism(ISO-RILEM)

PFA content		0%	10%			20%			30%		
Fly ash		--	**0**	**1**	**2**	**0**	**1**	**2**	**0**	**1**	**2**
Density (Kg/m^3)		2252	2234	2267	2268	2213	2265	2269	2194	2260	2269
Entr. Air		2.3	2.3	1.2	1.2	2.3	0.7	0.7	2.3	0.4	0.3
Total Air		2.3	2.7	1.3	1.3	3.3	1.0	0.8	3.7	0.8	0.4
Flexural strength (MPa)	1d	2.6	2.5	2.8	2.8	2.0	2.2	2.5	1.5	2.0	2.1
	3d	5.3	4.6	5.0	5.2	4.1	4.7	5.0	3.3	4.1	4.4
	7d	6.3	5.8	5.9	6.0	5.1	5.5	5.5	4.7	5.2	5.6
	28d	7.3	6.8	7.1	7.0	5.7	6.9	6.8	5.4	6.2	6.5
	56d	7.8	7.5	7.6	8.2	7.1	7.7	8.1	6.2	7.2	8.0
	91d	8.1	7.3	7.7	8.3	7.1	7.7	8.1	6.5	7.9	8.2
	356 d	8.6	8.8	9.5	9.4	8.5	9.0	9.2	8.5	9.6	9.8
Comp. strength (MPa)	1d	9.9	8.6	9.9	10.2	7.1	8.3	9.2	5.4	6.8	7.9
	3d	26.4	22.7	24.3	25.3	17.8	22.3	23.3	14.4	18.2	20.8
	7d	35.4	31.6	33.4	34.0	25.7	29.0	30.5	21.1	24.8	26.9
	28d	46.2	41.0	43.8	45.3	35.6	42.3	42.4	29.5	35.2	38.8
	56d	52.3	47.1	52.2	53.2	43.7	50.0	52.9	36.1	45.5	51.0
	91d	55.3	50.7	56.2	58.9	46.8	53.9	57.1	41.2	51.3	57.7
	356d	57.8	62.2	69.5	72.7	59.8	72.2	74.8	57.0	70.2	74.4

0 –as received fly ash (200 m^2/Kg Sp.surface), 1- fly ash (450 m^2/Kg Sp.surface), 2- fly ash (650 m^2/Kg Sp.surface)

Cheng and Osbaeck[15] studied the Effect of fly ash grinding on the hydration and strength development of fly ash cement and concluded that finer grinding of fly ash resulted in improved flowability of mortar and substantial improvement in compressive strengths as shown in Table-5

Chemical Activation

Chemically the reactivity of fly ash can be substantially enhanced by re-vitrification of fly ash mixed with varying concentration of soda ash, red mud or iron ore at 1300-1500^oC 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[16]. Also activation of fly ash by alkali helps to improve the compressive strength of the blended cements [17] . Fig. 6 shows the 1&28days compressive strength of PPC with unactivated and alkali(Low and high concentration) activated fly ash blended cement.

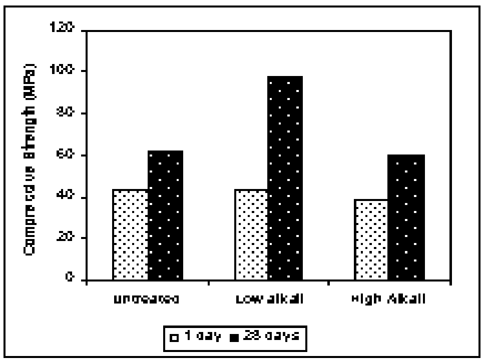

Fig. 6: 1&28 days Compressive Strength of alkali a activated cement

Processes for decreasing Combustibles:

The existing processes for removal of unburnt carbon rely mainly on physical methods , to separate combustibles in fly ash either by wet , dry or electrostatic processes , by froth flotation , vibratory methods, sieving, gravitational separation etc., but all these processes though technically feasible, they are commercially not viable due to economics. The need for power generators to comply low NOx emission regulations has lead most to install low NOx burners, which are effective at reducing NOx, but also results in an increase in unburnt carbon in fly ash. The presence of excessive carbon in fly ash adversely affect its properties and so its utilisation levels. So there is a need of a simple process in which carbon can be substantially and reliably removed from fly ash. This can be achieved through a good combustor or calciner [18] schematically as shown in Fig. 7. Experiments carried out at the authors laboratory have shown encouraging results , the process is techno-economically a feasible process .

Hamley et al [19] have reported a novel method for removal of unburnt carbon by a supercritical water oxidation (SCWO) process. The process have shown a reduction in combustibles up to 19-83% as shown in Table-6., furthermore the combustible removal efficiency was also linked to the reactivity of coals and needs optimisation of the process for the type of coal .

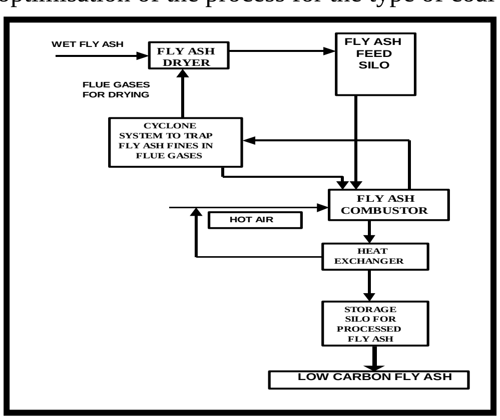

Fig. 7: Carbon Burn out process through a combustor

Identity & Country of origin of coal used	LOI before SCWO (% dry basis)	LOI after SCWO (% dry basis)	Reduction in LOI(%)
Ensham – Australia	7.64	4.56	40.3
Prodeco- Colombia	20.68	3.62	82.5
Kuzbass –Russia	4.37	3.54	19.0
Goedehoop – South Africa	12.37	6.14	50.4
Tyne Blend – UK	7.89	4.98	40.1
Bailey – USA	10.90	3.35	69.3
Guasare –Venezuela	22.56	4.73	77.9

Table-6: Loss on Ignition data for fly ashes before and after SCWO process

Ash Modified Clinker Technology (AMC):

A technology that can simultaneously reduce SO_2 emissions and create a marketable coal ash by-product for end-use markets (specifically the cement clinker market) where significant financial benefits can be realized by the technology, referred to as AMC technology [20] , is a worldwide patented process developed in China. Where a lime-rich powder with additives is added to coal at the coal pulverizer, increases the calcium oxide content of coal ash while the coal is burning by fusing calcium oxide to the ash. Calcium oxide in coal ash is a catalyst for coal combustion even under low-NOx boiler modes.
AMC technology [21] is particularly suited to value enhancement of coals that produce Class F fly ash with high-LOI and low-calcium oxide content under normal combustion mode or low-NOx burner modes. It is known that coal ash with high-calcium content (e.g. Class C fly ash) has many advantages. However, the calcium content of both anthracite and bituminous coals is very low, less than 5-10%. This low-calcium content limits the bonding characteristics of coal ash. Existing technologies cannot increase calcium content of both anthracite and bituminous coals; therefore increasing their cementitious bonding capacity and solving the coal ash recycle problem. AMC technology reduces carbon residue of fly ash and bottom ash after coal burning, therefore making these materials readily re-usable.
The cementitious clinker produced by this technology is having chemical composition as shown in Table- 7 and Table-8 illustrates the XRD analysis of AMC clinker with % phases formed and Table-9 gives the compressive and tensile strength values of cement from AMC clinker. Table-10 compares the AMC technology to FGD scrubber technology

Table-7 : AMC Fly ash clinker

LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
2.42	26.1	12.67	4.09	50.09	1.27	0.96	0.59	0.31

Table – 8 : XRD phases

XRD phases	% by Weight	XRD phases	% by Weight
Belite	35.2	mullite	8.3
Calcium aluminoferrite	4.9	Calcium silicate	1.6
Calcium carbonate	9.2	grossular	3.7
Undetectable crystalline or non crystalline amorphous phase			26.7

Table- 9 : Strength profile

	Compressive strength (MPa)	Tensile strength (MPa)
1 day	15.8	4.2
3 days	35.1	5.6
7 days	45.2	6.9
28 days	66.2	7.8

Table-10 : AMC technology v/s FGD scrubber technology [20]

	AMC Technology	FGD scrubber[1]
SO_2 reduction	Up to 90%	Up to 90%
Initial capital investment	$1.5 million [2]	$50 to $70 million
Annual O & M costs	$ 4 million [4]	$4.3 million
Downtime for tie –in	None	One week
By product of SO_2 reduction	Marketable clinker, high quality cement	Unmarketable FGD sludge
Use of by product	Sell: revenue $20 to $50/ mt	Dispose : cost $5 to $8 /mt
Other benefits		
• **Ash disposal**	Eliminated	$250,000/-year
• **Coal consumption**	Reduced 2%	No reduction
• **SO_2 emission**	Reduced	No reduction
1 – FGD scrubber data source: pollution & abatement handbook-part-III, Sulphur oxide prevention &control,1997, refers to wet throw way process		
2-Costs for the necessary equipment		
3- Includes the cost of AMC. Does not include the license fee to GNE		

Manufacture of sulphoaluminate Belite cements:

Calcium Sulpho-Aluminate–belite Cements are special variety of belite Cements [22] which are useful as repair materials and tailor-made grouting applications for specific applications. These cements have a capacity to tolerate higher levels of MgO contents (up to 10%) and so permit the usage of dolomite limestones [23]. As one of the main raw material, especially fly ashes from FBC(fluidized bed combustor) having relatively higher SO_3 content can find application in the production of special cements such as belite rich sulphoaluminate cement Beretka et al [24] and Maijling et al [25] have demonstrated such fly ashes could be used , thereby reducing CO_2 emission load to the atmosphere in the manufacture of these cements. Roy et al [26] demonstrated that sulphoaluminate clinkers with varying $C_4A_3\overline{S}$ and C_4AF with C_2S remaining more or less similar the compressive strengths achieved are shown in Table-11

Table 11 : Compressive strength of Sulpholauminate belite clinker [26]

	Potential Composition of clinker				**W/S**	**Compressive strength (MPa)**		
	C_2S	**$C_4A_3\overline{S}$**	**C_4AF**	**$C\overline{S}$**		**3d**	**7d**	**28d**
1	47.0	18.5	17.5	12.0	0.33	46.2	46.5	45.6
2	49.5	14.3	18.1	14.4	0.34	43.8	57.3	52.3
3	44.0	17.6	16.5	16.5	0.33	49.7	54.1	37.3
4	43.5	17.2	16.3	18.5	0.33	59.2	59.4	31.7
0	**OPC**				0.33	49.7	51.0	60.5

Other Options for Increased Fly ash Utilisation:

- **Ready Mix Concrete :** In India slowly the RMC concept is picking up, for large scale constructions. The growing awareness to produce a more durable structure has led to use mineral admixtures like fly ash in RMC for high Performance Concrete in Flyovers, high rise structures and other areas of applications of HPC . The advent of high volume fly ash Concrete pavements (using 40-50 % fly ash) in the country would result in substantial utilisation of fly ash and fly ash based blended cements for roads and pavements.
- **Fly ash for Bricks/ Blocks:** Clay bricks are not only used for housing purposes but also in infrastructure applications such as arch dam construction, irrigation works, pavements etc.. The need of the urban market for bricks is 60 billion and on national demand 160 billion[27]., thus depleting the fertile top soil for manufacture of clay bricks. With this backdrop the need of the day is bricks and blocks made with fly ash, it is proven technology with the quality of bricks comparable or better than clay bricks. Considering 25% penetration of fly ash bricks at national levels could consume ~45 million tonnes of fly ash ever year .
- **Manufacture of Zeolites:**
  Conventional synthesis of zeolites are based on hydrothermal crystallization of silicate and aluminate at relatively high pH. Indian fly ashes with high silica and alumina content could be a good alternative as raw material for zeolite production. These zeolites have multifaceted applications [28] such as
  - Suitable substitute for phosphatic builders in detergents
  - Catalyst in chemical/petrochemical industries
  - Adsorbent/ion exchanger in water /radioactive waste treatment
  - For electronics/mechanical industries

  The effect of alkaline solution on formation of Na-P type of zeolite was studied by Wang et al [29] where fly ash was subjected to processing for 24h with 1:10 W/S ratio in a relatively closed system. XRD indicated formation of various zeolites type like P,X & A, hydroxysodalite and a combination of these. Nugteren et al [30] synthesised Pure zeolites from silica extracts obtained from fly ash by alkaline leaching. The extraction potential of various types of European fly ashes was investigated under realistic process conditions (2 M NaOH; 90ºC; L/S=3; 4-10h.) and found to vary between 20 and 140 g of SiO_2 per kg ash, using a single step process. The formation of zeolites seems to be mainly influenced by the presence of Al in the liquid phase. Therefore, complexants for Al that are normally used in the Al anodising industry (sorbitol, gluconic acid, etc.) were added to the solutions with the aim of suppressing the crystallisation of zeolites.

❖ **Fly ash as source of Alumina:**

Simultaneous manufacture of alumina and cement clinker in another attractive process for enhancing fly ash utilisation. The alumina content in Indian fly ashes varies from 18-29%. Various scientists have reported[31]the attempts made for separation of Alumina. But the most used process is developed by Gryzmek [32] process of extraction of Alumina from fly ash and manufacture of cementitious binder as a byproduct. The schematic representation of the process is shown in Fig. 8

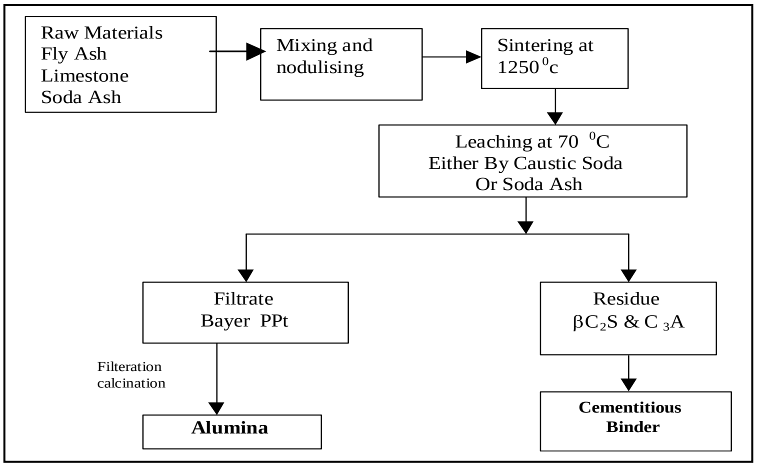

Fig.8 : Schematic representation of Gryzmek Process for Extraction of Alumina

The studies carried out at the authors laboratory have established the technical feasibility of the process , however the fly ash used in the process needs to have higher alumina content (>25%) for achieving the best results and a high purity of the alumina .

Technological options for Eco friendly Use of fly ash:

- **Green growing concrete:** a novel "Green-Growing Concrete" [33] has been developed in 1993 (US Patent No. 2981071). While this concrete has the strength and durability of conventional concrete, it can also support plant growth just like soil. This particular invention is becoming increasingly popular for river and Lake Embankment work, civil engineering work slopes, car parks and driveways. The Green-Growing Concrete Group has developed the technology for the effective use of fly ash as concrete aggregate, cement paste, filler and surface base material.
  The "Green-growing concrete" consists of two layers.
  1. A "porous concrete" layer, which is made by hardening aggregate with low-alkaline high-strength cement paste, has a porosity of 25 to 30 percent, is between 15 to 30 centimeters thick and has a compressive strength between 10 to 15 Newton per square millimeters.
  2. The second is a two to five centimeter-thick sprayed "surface base" layer, which is a combination of organic materials with high water and fertilization retentivity and resistance to erosion, and a mixture of fertilizer and seeds. "Green-fill," a filler mainly composed of organic materials, is used to fill the spaces inside the "porous concrete" to give it the necessary water retentivity and fertilization properties, and to neutralize the alkalis.

  The procedure involves first pouring the "porous concrete," second filling the "porous concrete" with "Green-fill" and third spraying "surface base" layer onto the "surface base" and planting. Grass or tree roots spread into the spaces inside the "porous concrete" and get nutrition from the "filler". The main features of this concrete are:
  - "Green-growing concrete" has the strength and durability of concrete, as well as the ability to grow plants like soil.
  - Planted bases that cannot be easily eroded by running water or rainwater can be built.
  - The concrete can be poured on-site, so this can be carried out according to the work surface conditions.
  - The concrete can also be pre-cast, enabling the work period to be reduced.
  - Not only can lawn or grass be grown on the concrete, but it can also take medium-sized trees.

Fig. 9 illustrates schematically the different layers of green growing concrete while Fig.10 shows the final view of green growing concrete .

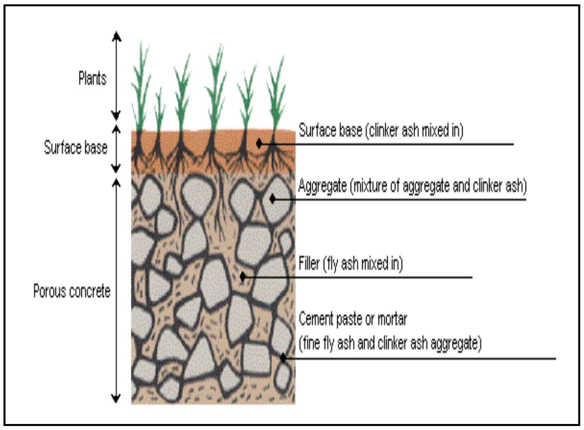

Fig. 9: Laying of Green Growing Concrete

Fig. 10 : Final view of layered Green growing concrete

SLASH Process:

Due to heavy metal concentration and pathogenic microbiological load, sewage sludge in South Africa is classified as toxic waste. Burnham et al [34] developed a process using either quick lime or kiln dust to effectively pasteurize sewage sludge, which is achieved either by maintaining pH above 12 for at least 7 days or alternatively ensuring a temperature in the range of 52-62 ^{0}C. based on these results Reynolds et al [35] developed a process based on fly ash called as SLASH process as artificial soil, where sewage sludge(60%), lime(10%) and fly ash(30%) is used. With varying proportions of the components fly ash can be used up to 60% in SLASH process. The results of microbial analysis as shown in Table-12, on the mix formulation indicated that at ~50 ^{0}C temperature the pathons were destroyed while some microbial activity was maintained. The survival of indigenous microorganisms is regarded as an advantageous for its use in agriculture, where they assist in establishing a soil ecosystem

Table- 12: Results of microbial for SLASH mixes [sewage sludge(60%), lime(10%) and fly ash(30%)]

Test	Initial count (colony forming units/ml)	Final count (colony forming units/ml)
Total aerobic bacteria	1.2×10^8	5.9×10^3
Escherichia Coli	2.4×10^5	6×10^0
Total coli forms	1.7×10^6	6×10^0
Faecal streptococci	4.8×10^5	Not detected
Parasites	2.0×10^0	Not detected

Various large volume batches of SLASH were used to ascertain the effect on different crops raised on various types of soil [36,37]. The trials conducted by raising the bed of soil and compared the production of spinach(vegetable) and asters (flower) using range of SLASH treatments. A mixture of 5% SLASH and 95% soil gave the best results for spinach, with 10% SLASH also similar results were observed, but with 30% SLASH although yield was more than untreated soil, it exhibited deficiency symptoms. Whereas in case of Asters, improved vigor was observed over control but all showed deficiency symptoms when SLASH was used 30%. Table –13 shows the response of asters flower plant growth and flowering characteristics of asters to different applications of SLASH. Authors concluded that optimisation levels of SLASH should take cognisance of both the original soil condition and crop requirement, apart from species difference, the end use also needs to be taken into account.

Table-13

% SLASH in medium	Plant height(cm)	Plant mass (g)	Number of flowers	Height of 1st flowering branch (cm)	Length of flowering branches (cm)	Total length of all branches (cm)
0	27	29	8	1	11	119
5	57	35	9	8	8	213
10	42	27	5	11	7	85
30	30	25	6	9	6	70

Potential Use of Fly Ash in Bedding on Dairies [38]:

From 1998, studies have been conducted at the Veterinary Medicine Teaching and Research Center (VMTRC) in Tulare, California and on nearby dairies to determine the potential uses of fly ash in bedding on dairies. The primary focus of these studies has been on the use of fly ash mixed with various types of manure bedding, to reduce bacterial populations in the manure bedding. The results indicated that by adding fly ash to manure bedding is of some benefit in reducing the bacterial load of the bedding. Significant reduction in coliform growth was noted when the mixture contained 15-25% fly ash and this reduction remained for up to 3 weeks. This level of fly ash in the mixture was associated with a pH greater than 10. It remains to the determined if this is an economic benefit or produces a reduction in cow diseases such as environmental mastitis. There appears to be no harmful effect on animal health from adding fly ash to bedding. Table 14 illustrates the distribution of bacterial growth (colonies/gm) on MacConkey Agar at various proportions of separator manure and fly ash mixtures.

Table-14 :

Fly ash:separtor manure	Lac+	Lac-	Small Lac-
75:25	0	0	0
50:50	0	0	0
25:75	0 – 1800	64,000 – 200,000	0
15:85	0 – 200	0	200
5:95	200	4000 – 8200	2000 – 36,000
0:100	100 – 120,000	20,000 – 200,000	18,000 – 2,000,000

Fly ash + gypsum (byproduct) mixtures , have been reported for use as manure , use of which has been reported to produce an increased yield of crops .

Fly ash from Captive Power plants

The present trends in Cement manufacturing plants in the country indicates that Captive power plants are going to be the common feature associated with cement manufacture. Most of these CPP would be designed to use higher ash coals. It needs to be mentioned here that a proper understanding and knowledge of the combustion process in these CPP, the fly ash generated could be produced of highly reactive nature tailor made to have desired properties, which could find its direct use in Blended Cements. This would thus not only lead to reduced power costs for the cement manufacture but effective utilisation the Fly ash produced would be an important add on benefit.

Conclusions:

To maximise the fly ash utilisation, the gap between usage level of 13- 15 % in India to an average target utilisation of 50% is huge. i.e use of ~ 40 – 50 million tonnes of fly ash as against current ~10-13 million tonnes of utilisation.

Some of the technological options discussed in the paper would help in achieving a substantial increase in the levels of utilisation of fly ash in different areas of its applications, the most promising ones could be:

- Technologies for enhancing the fly ash pozzalinicity
- Ash Modified Clinker Technology
- Use of HVFA pavements (a high priority application in the country)

These would substantially enhance the utilisation levels of fly ash in application areas such as infrastructural requirements of the country. From the angles of enviro-friendly applications of fly ash for forestations and greening the surroundings of metro cities, processes similar to the SLASH process and Green Growing Concrete would have immense applications.

Thus depending upon the location of the thermal power plant and choice of a proper technological option will lead to maximise the fly ash utilisation in the country.

Another catalysing action could be, if the thermal plants start looking at the fly ash produced as an important Byproduct and not as a waste product requiring disposal, along with the attempts of improving the energy efficiency of the thermal plants , if efforts are directed towards attempts on optimizing / improving the quality of fly ash produced , the objective and goal of achieving higher levels of fly ash usage in the country would not at all be illusive .

References:

1. Chand.. S.K. and Rao D.D.B.," Fly ash –Disposal or Utilisation?",Int. Conf.-Fly ash Disposal and Utilisation, CBIP, I-5,pp.35-41.
2. Chatterjee A.K., " Coal ash utilisation in the Indian cement and concrete industry –Present status and future opportunities"(private communication)
3. Kulkarni P.C.,.Kaduskar P.S,.Khadilkar S.A &.Cursetji R.M "Chemical-Mineralogical characteristics and assessment of reactivity of fly ashes of different source",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.
4. Karandikar M.V., Khadilkar S.A..and.Cursetji R.M., "Comparative Assessment of Pozzolanicity of Low Lime Class -F Fly ashes of Varying Amorphous Content " 5th Int. Sym. On Cement & Concrete , Oct. 28 to Nov.1, 2002, Shanghai, China.
5. Venkatesh D.S., Harish D.V., "Process the Fly ash for Beneficial Utilisation", Indian Cement Review Dec.1997, pp.25-28.
6. 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.
7. Hwang J. Y., Huang X., Gillis J. M., Hein A. M., Popko D. C., Tieder R. E. and McKimpson M. G., "Utilization of Low NOX Coal Combustion By-Products" www.netl.doe.gov/publications/proceedings/ 98/98ps/
8. Sorge, J.N., Hardman, R.R., Wilson, S.M., and Smith, L.L., "The Effects of Low Nox Combustion on Unburned Carbon Levels in Wall-Fired Boilers," 1993 Joint Symposium on Stationary Combustion NOx Control, EPRI and EPA, May 1993.
9. Newman, D.H., "Carbon Content Considerations in Ash Marketing Programs," DOE Third Annual Conference on Unburned Carbon of Utility Fly Ash, Pittsburgh, May 1997.
10. Matsufuji M., Kohata H., Tagaya K., Teramoto H., Okawa Y. and Okazawa S., " Study on properties of Concrete with Ultra-Fine Particles Produced from Fly ash", Proc, 4th Int. Conf. Istanabul, Turkey, May 1992, Vol-I,SP-132.pp.351-365.
11. Ziyi X., " Research on Superfine fly ash and its activity", Proc. of Beijing Int. Symp. Cement & Concrete, Beijing, China,1985,pp.493-507.
12. Paya J.., Monzo J.,.Borrachero M.V and Peris-Mora E., "Mechanical Treatment of Fly ashes Part-I: Physico-Chemical characterization of ground fly ashes", Cement and Concrete Research, Vol.25,No.7, 1995,pp.1469-1479.
13. Paya J.,Monzo J,.Borrachero M.V and.Peris-Mora E and.Gonzalez –Lopez E, "Mechanical Treatment of Fly ashes Part-II:Particle Morphologies in Ground Fly ashes (GFA) and workability of GFA-Cement mortars", Cement and Concrete Research, Vol.25,No.7, 1995,pp.1469-1479.
14. Monzo J., Paya J. and Mora E., " A Preliminary Study of Fly ash Granulometric Influence on Mortar Strength", Cement and Concrete Research, Vol.24,No.4,1994, pp.791-796.
15. Cheng h. Q. and Osbaeck B. " Effect of fly ash grinding on the hydration and strength development of fly ash cement"(private communication)
16. Garg S.K, Lal Kishen and Rehal S.S "Processing of flyash from a Captive Power Plant", Chemical Engineering World, Vol. XXX, No.12, Dec.95, pp. 155-157.
17. Arjunan P.,Silsbee M.R. and Roy. D.M., "Chemical activation of low calcium fly ash –Part-II: Effect of Mineralogical Composition on Alkali Activation"
18. Cochram J.W.and Wassel T.,"A Case Study : Carbon Burn -Out Plant For South Carolina electric & Gas",Energy Source News letter Fall 99.
19. Hamley P., Lester E., Thompson A., Cloke M and Poliakoff M., " Removal of Carbon from Fly ash using Supercritical water oxidation" www.flyash.org/2001
20. Put B., "Gold in Fly ash" ,Energy,Spring 2000,pp.25-28.
21. Oehr K. H. and. Naik T. R., "In-situ coal ash modification to a cementitious clinker", www.netl.doe.gov/publications/ proceedings/01
22. Associated Cement Cos. Ltd., " Product Brochure on CASAL", Bombay, India,1990.
23. Ali,M.M., Sharma, P.S. and et al, " Potentials of Using Dolomitic Limestone Sulfoaluminate Cement", Proc.9th Int. Congr. on the Chemistry of Cement, New Delhi, India,1992,Vol III, pp.227-232.
24. Beretka, J., Santro,L., et al, " Synthesis and Properties of Low Energy Cements Based on C_4A_3S", Proc. 9 th Int. Congr. on the Chemistry of Cement, New Delhi, India,1992,Vol III, pp.195-200.

25. Majling,J. and Roy,D.M., “ The Potential of Fly Ash for Cement Manufacture”, Am.Cer. Soc. Bull. 72, (10) 1993.
26. Roy,D.M., Silsbee.M.R. and Zaohui Xe “ Influences of surplus SO_3 in FBC ash on formation of belite rich sulphoaluminate clinker” www.flyash.org/1999
27. Bhanumatidas N and Kalidas N “ Programmes and policies of Fly ash Utilisation in India”, International Conference –Fly ash Disposal and Utilisation, CBIP,I-4, pp.28-34,.
28. Rayalu S.,Meshram S.U., Labhasetwar N.K., Biniwale R.,and Khanna P., “ New frontiers for high utilisation of fly ash: production of zeolites”, national seminar on Fly ash utilisation for value added products, Jamshedpur,Feb.1998,pp.83-89.
29. Wang H., Zhang Q., Song C., Liu F., “Synthesis of Zeolites by Alkaline Activation of Fly Ash” Journal of University of Science and Technology Beijing (English Edition), Volume 8, Number 3, Sep 2001,pp.161.
30. Nugteren H. W., Moreno N., Sebastia1 E. and Querol X., “Determination of the Available Si and Al from Coal Fly Ashes under Alkaline Conditions with the Aim of Synthesising Zeolite Products”
31. “Detailed Project Report Of Task Force On “ High Value Added Products From Fly Ash”, Fly Ash Utilisation Group Central Power Research Institute. P.B.No. 9401, Bangalore - 560097
32. Gryzmek J., “The Complex Alumina And Cement Production By Sinter Desintegration Method” Polservice Foreign Trade Enterprise Chatubinskiego 8 , 00 – 613 Warszawa Poland.
33. "Green-growing concrete" (Patent No. 2981071) –Takenaka *e* Report 2001. Takenaka corporation
34. Burnham J.C,Hatfield N., Bennett G.F and Logan T.J., In:Innovations and uses for lime”, ASTM STP 1135 (Eds.D.D.Walker,Jr.,T.B.Harddy,D.C.Hoffman and D.D.Stanely) American Society for Testing Materials, Philadelphia,1992.
35. Reynolds K., Kruger R. and Rethman N., “ The Manufacture and Evaluation of an artificial Soil (SLASH) prepared from fly ash and sewage sludge”www.flyash.info.
36. Rethman N.F., Reynolds K.A. and Kruger R. A.,1999 International ash utilisation symposium,Lexington, Kentucky
37. Rethman N., Reynolds K.A. and Kruger R. A. Ramagadza E.J. and Du Toit E.W., , , “ SLASH” for flower and vegetable production in the informal sector in south africa" 1999 International ash utilisation symposium, Lexington, Kentucky
38. Brazil L., Kirk J., Finger R., Holmberg C., Sischo W. and Higginbotham G. “Studies on the Potential Use of Fly Ash in Bedding on Dairies” www.vetmed.ucdavis.edu/vetext/