Environment Friendly Utilization of Fly Ash

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Introduction:

Most the world-wide of energy (88%) is produced by the combustion of fossil fuels like oil, natural gas and coal. All of these fuels are composed of major constituents such as carbon, hydrogen and oxygen and other components including sulphur and nitrogen compounds and metals. During the combustion process, different pollutants are emitted such as fly ash (containing diverse trace elements (heavy metals)), SO_x (SO_2 and SO_3), NO_x (NO_x = NO + NO_2) etc. Air pollution caused by particulate matter and other pollutants not only directly impacts the atmospheric environment but also contaminates water and soil, leading to their degradation. The exhaust gases released into atmosphere are irradiated by ultraviolet (UV) sunlight and undergo photochemical transformations. Wet and dry deposition of inorganic pollutants leads to acidification of the environment. These phenomena affect human health, increase corrosion and destroy crops and forests.

In the last few years, India has seen a remarkable growth rate and the founding stones upon which this growth triumphs is the power generation capability of our country. There are various sources of power generation viz. Coal, Gas, Hydro, Nuclear, Wind and other renewable sources. But among these various sources of power generation, coal is still the major part, with more than 65% of dependability on coal and natural gases. Percent wise installed capacity with various sources in India is shown in **Fig (1)**

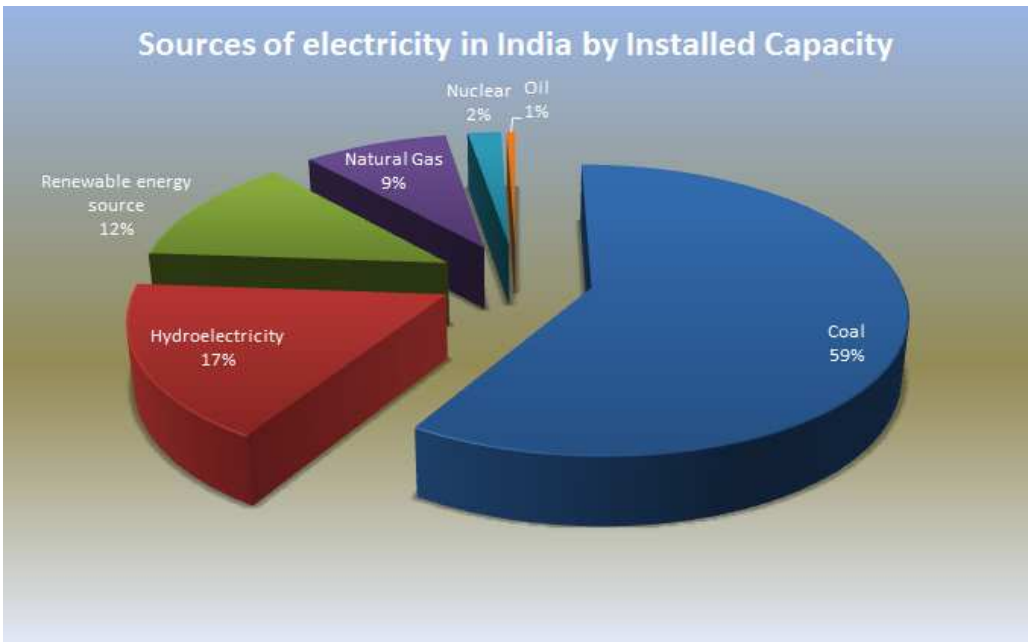

Fig (1): Various sources of power generation in India

From the beginning all coal based thermal power plants in India are facing two major challenges. If we take the typical example of NTPC Vindhyachal (VSTPP) that has installed capacity of 4760 MW (6x210 MW, 7x500 MW) and it is the biggest thermal power plant of India as on date. Two major challenges that this plant is facing are:

(a) Ash Utilization: The typical Indian coal which is being used for power generation is of lignite or sub-bituminous in nature and contains 30-45% of ash content. So after combustion of this coal in power plants huge amount of fly ash is generated as a bi-product. Utilization of this huge amount of fly ash is a big challenge for coal based thermal power plants. We have to look beyond the conventional ways and think some innovative ways for the utilization of fly ash. In recent time there is increasing trend of capacity power addition with more and more coal combustion which will ultimately result in more and more fly ash generation. So it's a matter of great concern to look into it, as how to improve upon ash utilization keeping in view of power addition in India.

(b) Environment Norms: Environmental norms are getting stringent day by day. To curb the SO_x emission, Flue Gas Desulphurization (FGD) unit needs to be installed in every 500 MW units in India. As per the recent norms shown in **fig (2),** every new 500 MW or more units will necessarily have the FGD unit for the minimization of SO_x. As far as NO_x is concerned it is under limit at NTPC, VSTPP as per the recent norms, [see **fig (3)**] but with time it will also come under more stringent policy and we have to think for the minimization of NO_x emission as well. Also it is our social as well as moral responsibility to think about our environment and take proper steps to reduce emission impact upon environment.

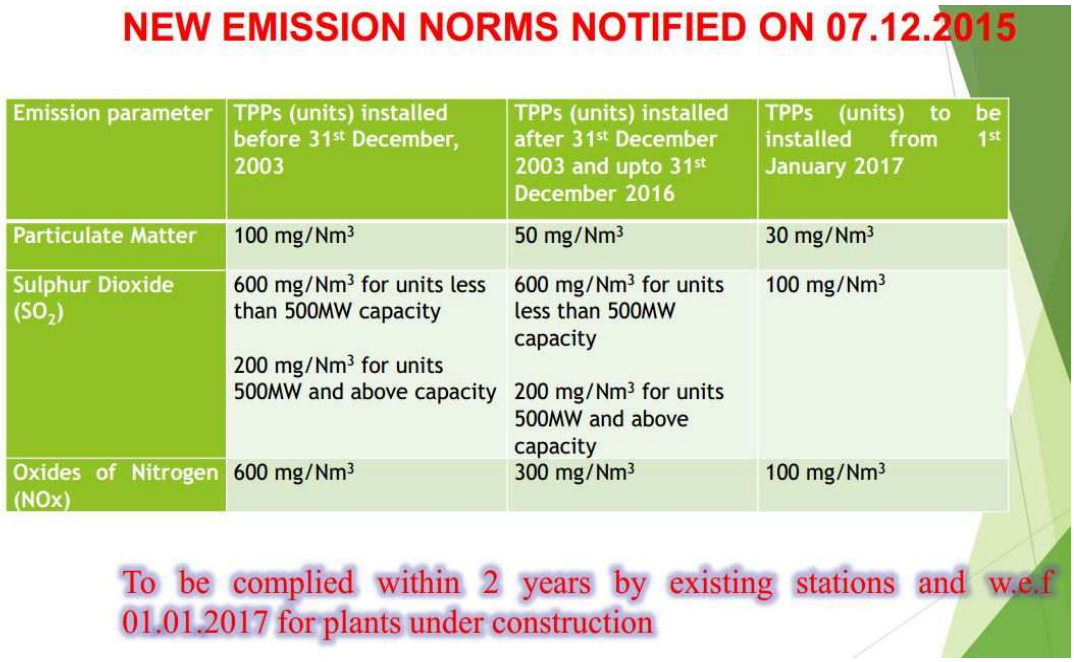

Fig (2): Recent Environment Norms issued by MoEF

Parameters	New Std	210 MW	500 MW	Remarks
PM	100	150	100	R&M works in St-I & St-II under progress
SOx	600 (<500MW) 200 (500 & above)	<600	>600	St – I within limits. St – II, III & IV requires FGD unit
NOx	600	<600	<300	Already within limits

Fig (3): Environmental parameters at VSTPP for various units

Current FGD system:

The FGD system being commissioned at stage V of NTPC Vindhyachal is of limestone based wet FGD and it requires lot of space and infrastructure. In the process it produces the end product Gypsum which is also a chemical burden with low economic value. At VSTPP, FGD system is under advanced stage of commissioning, but we are still in search of buyer for the end product Gypsum. Also procurement and handling of such a large amount of limestone and gypsum produced is a tedious job. Annually almost 2.0 crores value of Limestone is needed for a 500 MW unit. A typical flow diagram of wet FGD is shown in **fig (4)**

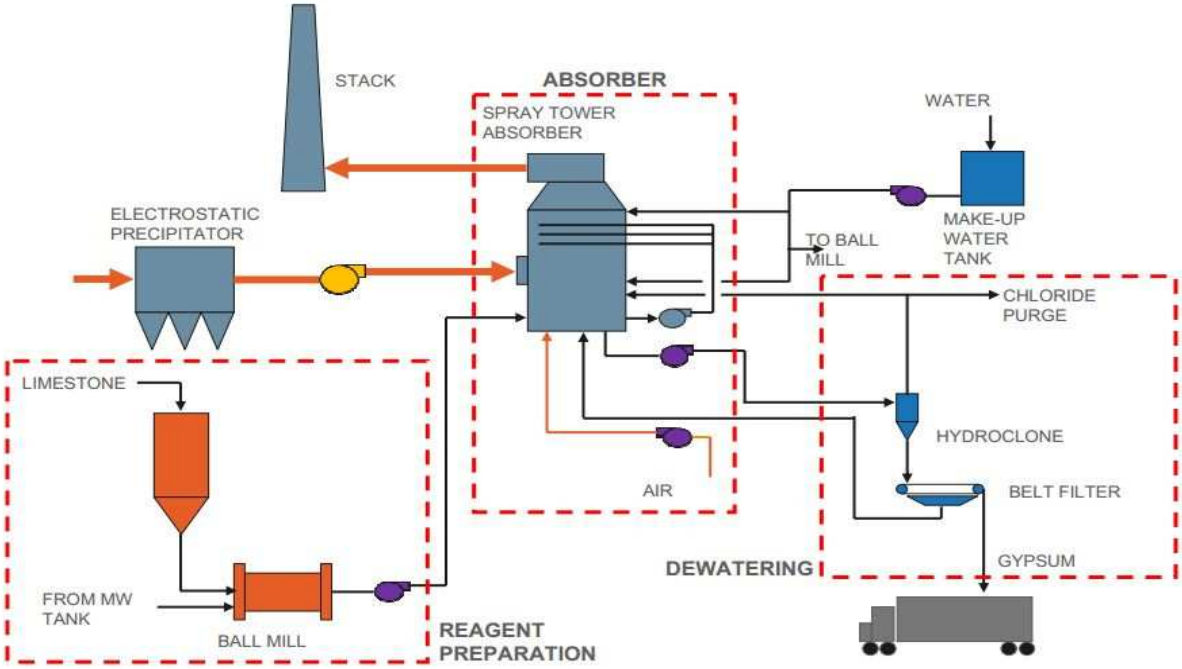

Fig (4): Typical Flow diagram of wet FGD system

Our Approach:

In view of the above challenges, we suggest an innovative and environment friendly approach to utilize the fly ash which will curb the emission of SO_x as well as NO_x and end up with a bi-product which is in house useful liquid coagulant.

Here we suggest an Electron-beam method of flue gas treatment (EBFGT) technique where we will be using the most challenging waste for any coal based thermal power plant i.e. fly ash and SO_x/NO_x derived from flue gas to form a reaction mixture which after the reaction gives us a clear form of liquid which acts as excellent coagulant for the treatment of raw water, waste water and also sewage water. Presently we are using ferric alum and PAC as a coagulant for which we nearly spend 1.5-2.0 crores per annum at NTPC Vindhyachal.

Electron-Beam method of Flue Gas Treatment (EBFGT):

Among conventional technologies for flue gas treatment aimed at removal of SO_2 and NO_x are wet, dry and semi-dry flue gas desulfurization (FGD) and selective catalytic reduction (SCR) of NO_x.

Electron Beam Flue Gas Treatment (EBFGT) technology is among the most promising advanced technologies of new generation. This is a dry-scrubbing process of simultaneous SO_2 and NO_x removal, where no waste, except a by-product, is generated. The application of electron beam irradiation to initiate chemical reactions to remove SO_2 and NO_x was first investigated by joint research of the Japan Atomic Energy Research Institute (JAERI) and Ebara Corporation in the early 1980s. A high irradiation dose is required for NO_x removal, while SO_2 is removed in proper conditions at low energy consumption.

The method has been developed since then, from the laboratory to pilot and a large demonstration scale by research and development projects in Japan, USA, Germany, China and Poland. The final engineering design technology for industrial applications was achieved at pilot plants operating in Nagoya, Japan and at Kawęczyn, Poland. EBFGT technology for coal-fired boilers has been implemented on an industrial scale at the Thermal Power Plants (TPPs) at Chengdu and Hangzhou in China and at the EPS Pomorzany in Poland. At present, the EBFGT installation in Poland is the only operational installation in the world. **Table (1)** presents the main parameters of these installations. The plants in China were designed mainly for SO_2 removal, while the plant in Poland was designed for simultaneous SO_2 and NO_x removal. The flue gases from two Benson boilers (65 MW (e) and 100 MW (th) each)) are purified at the EPS Pomorzany in Poland. The maximum flow rate of the gases is 270000 Nm^3/h and the total electron beam power is equal to 1 MW. There are two process vessels over which two electron accelerators are installed in series (700 keV, 260 kW each). The applied dose is in the range 7–12 kGy (kJ/kg). At these doses, the removal efficiency approaches 85–95% for SO_2 and 50–70% for NO_x.

Table 1. Main parameters of industrial EB installations

Parameter	Unit	Chengdu TPP, China	Hangzhou TPP, China	Pomorzany EPS, Poland
Flue gas flow rate	Nm^3/h	300 000	305 400	270 000
Inlet flue gas temperature	°C	150	145	140
Inlet SO_2 concentration	mg/Nm^3	5150	2770	2000
Inlet NO_x concentration	mg/Nm^3	820	410	600
SO_2 removal efficiency	%	80	85	90
NO_x removal efficiency	%	18	55	70
EB		800 keV, 320 kW×2	800 keV, 320 kW×2	700 keV, 260 kW×4

We are proposing following steps for Electron Beam Flue Gas Treatment using fly ash slurry. Flow diagram is shown in **fig (5)**

Step 1: In this method the flue gas from ESP outlet is passed through a spray cooler for cooling with sprinkling water.

Step 2: It is subjected to Electron beam chamber where due to bombardment of electron beams NO_x and SO_x get oxidised due to free radical formation.

Step 3: Afterwards this flue gas is reacted with ash slurry for the period of four hours in absorber tank. There is provision of two absorber tanks. One will be in service for four hours and other will be standby. Once the reaction for four hours completes the other absorber will be taken into service and reaction mixture of first absorber is sent to settling pond. In this way continuous flow of flue gas is achieved.

Step 4: Reaction mixture is sent to settling pond. In this pond after settlement of undissolved particles clean supernatant is formed this is actually the liquid coagulant. This coagulant is formed due to reaction of Al_2O_3 and Fe_2O_3 from fly ash with SO_x.

The reactions are described as follows. Fe_2O_3 and Al_2O_3 in fly ash react quickly with the H_2SO_4 formed to produce Fe^{3+} and Al^{3+} (reaction 1 and 2).

$$Fe_2O_3 + 6H^+ \longrightarrow 3H_2O + 2Fe^{3+} \quad (1)$$

$$Al_2O_3 + 6H^+ \longrightarrow 3H_2O + 2Al^{3+} \quad (2)$$

At the same time, $KClO_3$ oxidises SO_2, resulting in additional $SO4^{2-}$ and H^+

$$KClO_3 + 3H_2O + 3SO_2 \longrightarrow 3SO_4^{2-} + 6H^+ + K^+ + Cl^- \quad (3)$$

Hydrolysis (4, 5, and 6) follows with hydroxides from water dissociation,

$$H_2O \leftrightarrow H^+ + OH^- \quad (4)$$

$$2Fe^{3+} + (6-n)/2\ (SO_4^{2-}) + n(OH^-) \rightarrow Fe_2(OH)_n(SO_4)_{(6-n)/2} \quad (5)$$

$$2Al^{3+} + (6-m)/2\ (SO_4^{2-}) + m(OH^-) \rightarrow Al_2(OH)_m(SO_4)_{(6-m)/2} \quad (6)$$

Polymerization (7 & 8) will proceed under certain conditions to form polymeric ferric sulphate (PFS) and polymeric aluminium sulphate (PAS), two components of the complex polymer.

$$p[Fe_2(OH)_n(SO_4)_{(6-n)/2}] \rightarrow [Fe_2(OH)_n(SO_4)_{(6-n)/2}]p \quad (7)$$

$$q[Al_2(OH)_m(SO_{4)(6-m)/2}] \rightarrow [Al_2(OH)_m(SO_4)_{(6-m)/2}]q \quad (8)$$

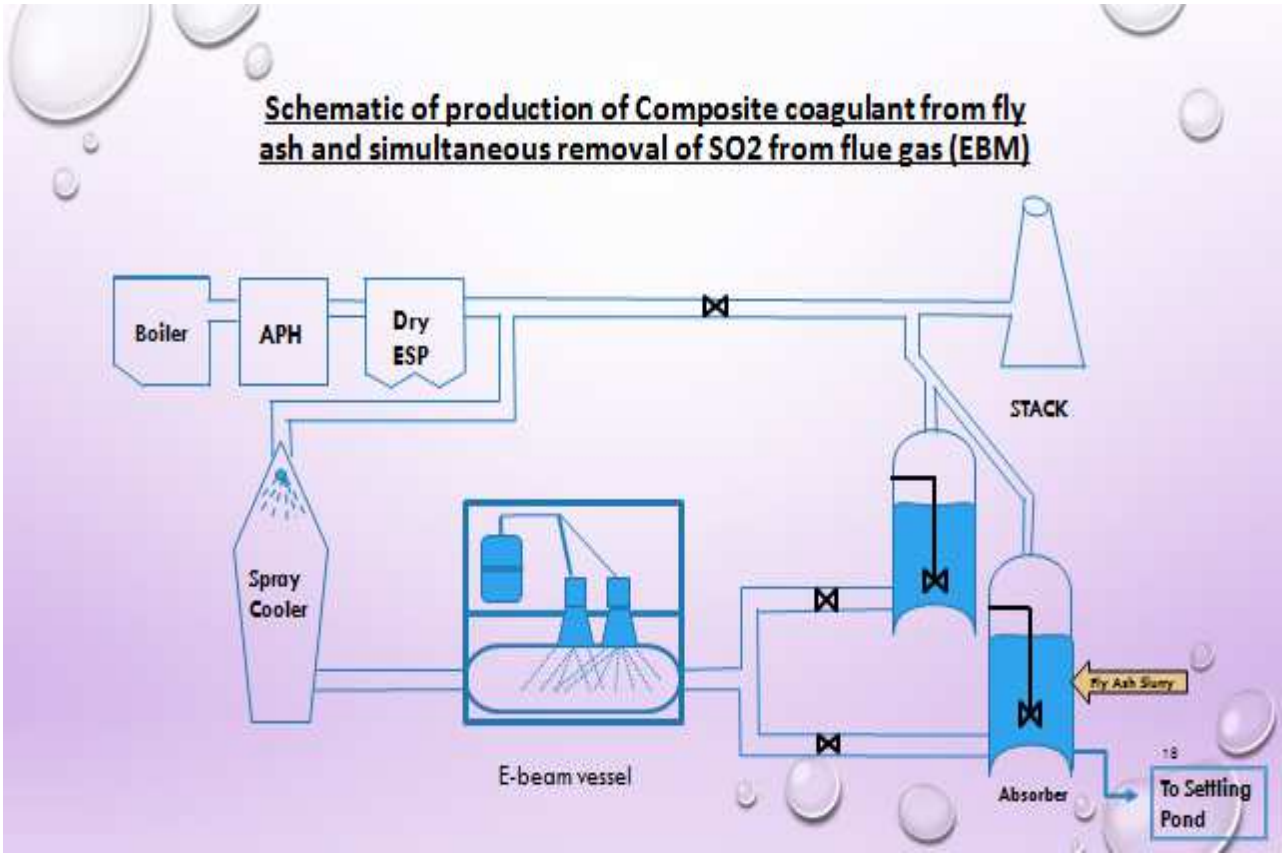

Fig (5) Typical Flow Diagram of removal of SOx/Nox from flue gas by E-Beam method

Experimental Work:

We have prepared this liquid coagulant (complex polymer) at our lab by reacting in situ the flue gas of unit 10 (at 380 MW) at NTPC Vindhyachal shown in **Fig-7a** with slurry of fly ash and measured the SO_2 content in flue gas and found that it is absorbing the SO_2 from flue gas. A graph is plotted with time in the graph **7(b)**.

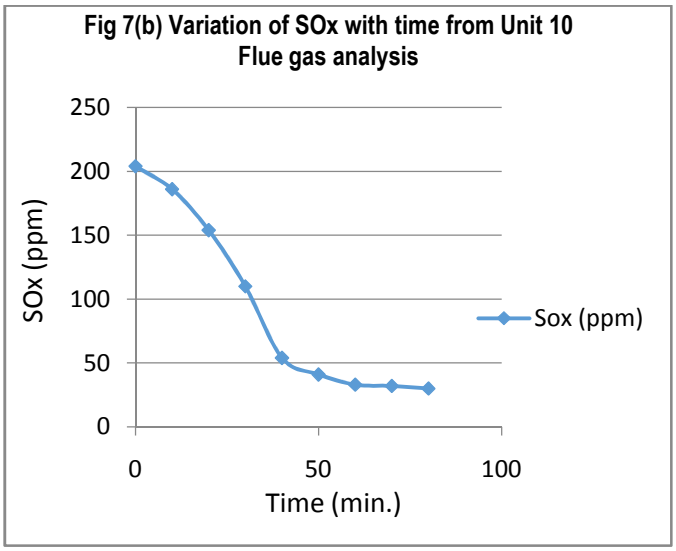

Fig 7(a) Reaction of Flue gas with Ash Slurry

We didn't have electron beam source so we used an oxidiser $KClO_3$ for the oxidation of SO_2 to SO_3 for the better reaction. In a same way we tried the same reaction at our lab with the help of 1000 ppm SO_2 cylinder and we found that the fly ash slurry is absorbing considerable amount of SO_2 during the process plotted in **fig 8(b)**. Lab set up and graphical illustration is shown in **fig 8(a)** and **8(b).** We couldn't do much quantitative estimations due to our lab restrictions. Only we could measure the SO_2 with time coming out of reaction mixture and found considerable dip in SO_2 value.

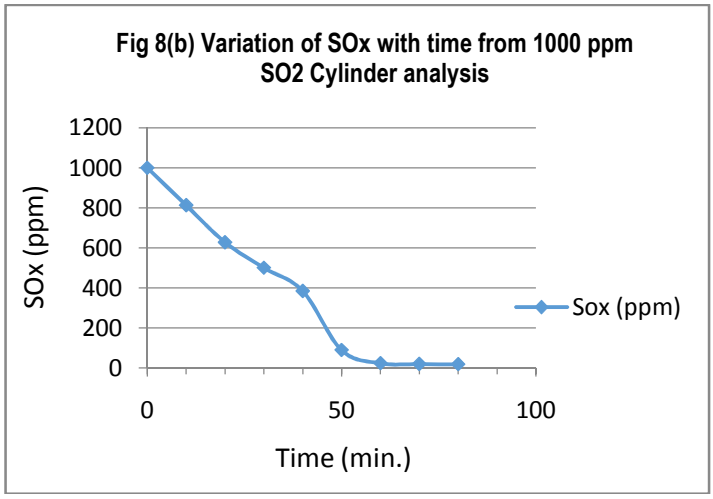

Fig 8(a) Reaction with 1000 ppm SO2 Cylinder

We used 500 gm of fly ash for our reaction. Reaction took place only upon the availability of Al_2O_3 and Fe_2O_3 component from fly ash. But we assume when continuous supply of fly ash slurry is maintained the absorption of SOx with time will improve. Initially the reaction rate is more but with time when reactive part of fly ash is consumed the rate gets decreased and at the end reaction rate is lower as reactive part concentration is low here hence there was part of saturation in (**Fig 7(b) & 8(b)**). It needs further investigation to find out the rate of reaction and quantitative measurement of SO_x absorbance from flue gas. There is not much difference in both the reactions (**Fig 7(b) & 8 (b)**) in the case of flue gas and 1000 ppm SO2 cylinder. We found that reaction rate is higher in the case of cylinder as initial concentration of SO_2 is higher in this case while it was comparatively low in flue gas.

From our lab finding it is very clear that our power plant fly ash has a capability of absorbing SO_2 and converting it into a coagulant. Also with the help of our lab scale reactions we found that almost 5-10 % of fly ash is getting consumed in the formation of liquid coagulant.

Composite Coagulant:

After the reaction of fly ash and oxidised flue gas, the product is a coagulant .We compare this coagulant in our lab and find it better than alum. We check its coagulating power, pH and heavy metals in the coagulant and found it comparable with the conventional coagulating agents like alum, PAC, poly-electrolytes etc. We took two different types of waste water having turbidity more than 1000 NTU from Liquid Waste Treatment Plant (LWTP) and Coal slurry Settling Pond (CSSP) respectively to treat it with various concentration of our lab prepared coagulant and found 0.5 ppm dosing of liquid coagulant is the best, through Jar Test and treated water has Turbidity below 10 NTU which is shown in the fig **9(a)** and **9(b)**

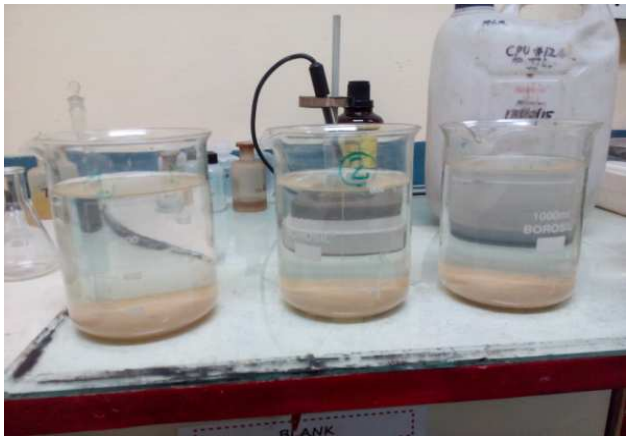

Fig 9(a) Treated water from LWTP

Fig 9(b) Treated water from CSSP

Advantages:

10% of fly ash consumption: If we calculate the total utilization of fly ash for a typical 500 MW unit considering 90% PLF and 35% of ash and 0.45% of sulphur content in coal, we find that in a day almost 200-250 MT of fly ash can be consumed to form the liquid coagulant, i.e. almost 10 % of total fly ash generated in a day from 500 MW unit.

For a typical 500 MW Unit, if

PLF = 90%, Coal flow = 288 TPH,

Ash produced per day= 7000*35% = 2450 MT,

If S in coal = 0.45%, SO2 flow = 2.46 TPH

SO_2 production per day = 60 MT

To consume this SO_2 required Al_2O_3 & Fe_2O_3 = 208 MT

Considering 10% reaction total Fly Ash required (approx)= 2000 MT

Total ash converted into coagulant ≈200 MT i.e 8-10% of total ash produced

Simultaneous removal of NO_x,: Limestone based FGD being installed at VSTPS is removing only SO_x. While by E-beam method NO_x can be removed. We didn't have E-beam source hence we could not do experiments for NO_x removal.

Total Savings: cost of chemicals used as coagulants (2 crore) + cost of limestone required in FGD (2 crore) – sale of by-product /Gypsum (1.5 crore) = 2.5 crore per annum.

In-house consumption of end product: Liquid coagulant produced is very much useful for every power plant for the treatment of various waters used in plant**.** It plays very vital role in producing quality DM water for the production of steam. Also lot of water is required for condenser cooling that needs to be treated with coagulant. The coagulant plays vital role to achieve Zero Water Discharge, a statutory requirement for every power plant now a days.

Reduced Aux Power Consumption: with reduced APC (N) our ECR will come down, giving us competitive advantage.

Conclusion:

With our findings and literature surveys we conclude that electron beam method for flue gas desulfurization is very promising technique and many countries like USA, China, Japan and Poland are using this technique in their coal based thermal power plants. In India it is still to be explored and keeping in view of the future demand of power in India this technique has right potential to solve the environment related problems in the form of fly ash and SOx/NOx emission that arises due to power generation form fossil fuel like coal.

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