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A RESEARCH ABOUT DIFFERENT USABILITY OF FLY ASH AND ULTRAMARINE PIGMENTS: A CASE STUDY OF SOLID-STATE CHEMISTRY

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A Research about Different Usability of Fly Ash and Ultramarine Pigments: A Case Study of Solid-State Chemistry

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Abstract* – *Ultramarine pigments were effective combined from zeolite An acquired from kaolin waste. This waste has been utilized as a magnificent source of silicon and aluminum for zeolite synthesis on account of its high kaolinite fixations and low substance of other frill minerals. The expense is naturally not exactly the industrialized item. Color added substances (Sulfur and Sodium Carbonate) were blended with different extents of zeolite An and further calcined for 5 h at 500 °C. They were portrayed by XRD and XRF notwithstanding visual classification by color and shade. These items show colors from blue to green at different shades, both impacted by the measure of added substances and cooling rate after calcination. In this manner, a different amount of the same added substances in the same zeolitic matrix gives an expansion in the color power. Cooling rate after calcination incites the color change which is considerably imperative in the pigments generation.

Fly ash had the benefit of being formless, though the customary beginning reagent, kaolin, should have been warmth treated before the ultramarine synthesis to debilitate its structure. A correlation of the scanning electron micrographs of fly ash, fly ash treated at 1 000 °C, fly ash responded with sodium carbonate at 860 °C and the ultramarine items demonstrated that sulfur had a structure-coordinating impact.

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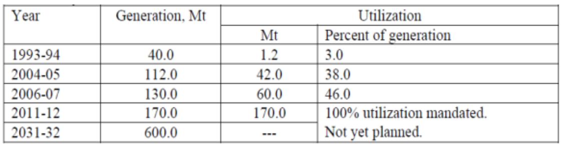
INTRODUCTION

The thermal power plants in India are essentially reliant on the combustion of high-ash bituminous coal in pummeled fuel fired frameworks. Pounded lignite fired boilers and pressurized fluidized-bed combustion frameworks are in operation to a constrained degree. Consequently, the low-lime fly ash (like Class F of ASTM C 618) is the prime assortment produced in India, albeit fundamentally littler volumes of high-lime fly ash (tantamount to ASTM Class C) and PFBC fly ash are accessible in the nation. This study makes an endeavor to catch the physico-chemical attributes of the Indian fly ashes, their standard example of utilization, issues and prospects of more current applications, present methods of value upgradation including mechano-chemical enactment and their prospects and confinements.



Year	Generation, Mt	Utilization	
		Mt	Percent of generation
1993-94	40.0	1.2	3.0
2004-05	112.0	42.0	38.0
2006-07	130.0	60.0	46.0
2011-12	170.0	170.0	100% utilization mandated.
2031-32	600.0	---	Not yet planned.

Table 1. Fly Ash Generation and Utilization in India.

Various methodologies have been made for the use of fly ash either to decrease the expense of transfer or to minimize its effect on the earth. FA has discovered utilizations in the cement and concrete industry as an added substance, treatment of corrosive mine seepage and also in area recovery and reclamation (Ahmaruzzaman, 2010; Gitari et al., 2008; Vadapalli et al., 2008;). In any case, it was found that one way to deal with diminish the contamination from FA is to change over the waste FA into high esteem zeolites. Zeolites are crystalline hydrated aluminosilicates of soluble base and basic earth cations with three-dimensional silicate structures. Various assortments of zeolites happen in nature, in any case, amidst the most recent century it was found that zeolites could be incorporated in the research facility. The soonest contemplates on the synthesis of zeolites were directed by Richard Barrer and Robert Milton in the late 1940`s. As indicated by Cundy (2005), Barrer started his studies by examining the transformation of known mineral phases under the activity of a solid salt arrangement at genuinely high temperatures i.e. around 170 to 270 °C. Notwithstanding, Milton spearheaded the utilization of more receptive antacid metal aluminosilicate gel at low temperatures (100 °C) and autogenous weight. The vital beginning materials used to blend zeolites are silica and alumina which are hydrothermally treated with a metal cation arrangement. Zeolite synthesis was ordinarily created by hydrothermal crystallization under antacid conditions, which has been accounted for by a few licenses and specialized articles. As of late, the classic soluble hydrothermal synthesis has been enhanced by utilizing more advanced treatments, which incorporate an antacid combination step followed by hydrothermal treatment, the use of microwave-helped zeolite synthesis and a method for orchestrating zeolites under liquid conditions with no expansion of water (Reyes, 2008).

LITERATURE REVIEW

Fly ash is a fine-grained inorganic powder residue which is composed of spherical glassy particles which are derived from minerals produced during the combustion of coal. It appears grey in colour, abrasive, mostly alkaline and refractory in nature. It consists of inorganic, incombustible matter present in the coal that has been fused during combustion into a glassy, amorphous structure. According to Scheetz & Earle (1998), fly ash particle size normally ranges from 0.5 to 200 µm and is mainly composed of amorphous aluminosilicate glass, crystalline phases (such as quartz, mullite, hematite, lime and magnetite) together with varying amounts of iron, sodium, potassium, calcium, titanium, sulphur, carbon and magnesium (Wang and Wu, 2006).

Fly ash is carried off in the flue gas as it leaves the combustion chamber and is usually collected from the flue gas by means of electrostatic precipitators and in some cases by bag houses, or mechanical collection devices such as cyclones (Scheetz and Earle, 1998). The formation of fly ash during combustion of coal consists of a series of complex mechanisms to form each constituent of the ash and is determined by a vast amount of factors.

Knowledge of the physical characteristics, chemical composition and properties of fly ash is essential to understanding any possible environmental impacts. Chemical and physical properties of fly ash vary greatly (.i.e. from one sample to the next) as a function of the coal source, type of coal burnt, the boiler used and its operating conditions and the process undergone by coal before combustion (Vassilev and Vassileva, 2007). Although fly ash varies from sample to sample, some generalisations can be made in terms of the physical, chemical and mineralogical characteristics.

According to Byrappa and Yashimura (2001), the channel system in various zeolites is formed by different combinations of linked rings in the tetrahedra. The size of the cation that can be introduced into the zeolite structure is dependent on the size of the channels (Byrappa and Yoshimura, 2001).

Querolet al. (2001) studied the utilisation of zeolites derived from fly ash in the wastewater and flue gas decontamination. Their study revealed that zeolites have a high affinity to NH4+ ions in the wastewater, but the efficiency of the NH4+ uptake was affected by the presence of other impurities and ions in the wastewater.

Malhotra and others (2002) report on the use of fly ash in America in 2002. They estimate that only 30 % of the fly ash produced is used. Two thirds is used in the concreteindustry, which has reached a maximum consumption figure. Malhotra and others challenge researchers to find low cost but high volume applications of fly ash, and to convert ashes into value-added products.

According to Feijenet al. (2004), water molecules also enhance crystal growth by filling the void spaces, which stabilises the zeolite structure. Previous studies have shown that increasing the liquid to solid ratio during the hydrothermal synthesis of zeolites from FA increases the dissolution of mullite, quartz and the glass matrix. As a consequence, the yield of zeolites also increases. For most synthesis procedures, de-mineralised water is used to avoid the complicating effects of competing ions such as calcium, which are commonly present in tap waters.

Buhler and Cerato (2007) used lime and Class C fly ash to reduce the plasticity of highly expansive clays. Soil samples with similar classification were used to show shrinkage variability with the addition of lime and Class C fly ash. The plasticity reduction was determined with linear shrinkage test. The results showed that both lime and fly ash reduced the linear shrinkage but the addition of lime caused further decrease in linear shrinkage. The high unit weight of fly ash relative to lime has made its lag in shrinkage reduction. So, we needed less lime than fly ash to reduce the plasticity of a highly expansive soil whereas fly ash is a waste product of power plant and it is more cost effective than lime.

Scheetz and Earle(2008) comment on the use of fly ash in America. Only 27.4 % of the ash produced in 1996 was used in non-landfill applications (confirmed by Hower and others7). Scheetz and Earle12 challenge researchers with the following remark: ...[Fly ash] was imparted with an excess energy, either chemical or stored surface energy, which can be utilized to participate in chemical reactions, if properly activated. The challenge for the scientific community is to exploit these resources, as low tech materials, to solve large-volume societal-environmental needs.

Belvisoet al. (2010), distilled water and seawater were used during the hydrothermal synthesis process in separate experiments. The findings of these studies indicated that zeolites can be synthesisedfrom different kinds of coal FA under low crystallisation temperatures using both distilled water and seawater.

In addition, the study showed that X-type zeolite, ZK-5-type zeolite and hydroxysodalite can be synthesised at lower temperatures when using seawater, whereas A-type zeolite could be synthesised only when using distilled water (Belvisoet al., 2010).

Lin et al. (2013) studied two expansive soils from a microscopic point to better understand the cation exchange capacity, mineralogical, and microstructural changes that occur during Class C Fly Ash stabilization. X-ray diffraction (XRD) was used to monitor the mineralogical changes and scanning electron microscopy (SEM) was adopted to observe the microstructural alterations. Energy Dispersive X-ray Spectroscopy (EDXS) was used to evaluate the distribution of the stabilization agent inside the specimen. It was found that the CFA stabilization process reduced the plasticity index (PI), clay size fraction, percent of swell, swell pressure, and volumetric water contents of the soil water characteristic curves, and increased the unconfined compressive strength. The reaction between soil and fly ash caused the iron-oxide coating that verified by both XRD and energy-dispersive X-ray spectroscopy analysis. The combined effects of flocculation and coating reduced the water-retention property of the stabilized soils, decreased their swell potential, and increased the soil strength.

Prasad and Sharma (2014) evaluated the effectiveness of clayey soil blended with sand and fly ash for soil stabilization by studying the subgrade characteristics. The purpose of this work is to find a solution for proper disposal of fly ash and also provides good subgrade material for pavement construction. The results showed that substantial improvement in compaction and California bearing ratio of composite containing clay, sand and fly ash. The swelling of the clay also reduced after stabilization. The maximum dry density of clay-sand-fly ash mix decreased with the addition of fly ash and optimum moisture content increased. Thus the stabilized soil can be used for construction of flexible pavements in low traffic areas.

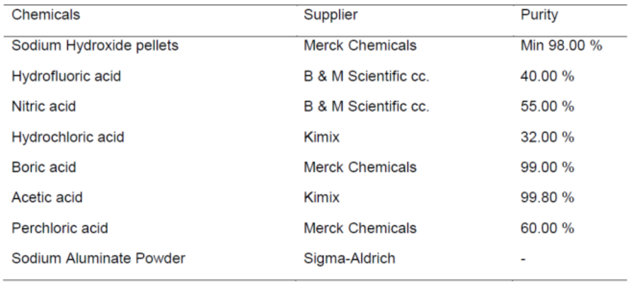
METHODOLOGY

SYNTHESIS OF ZEOLITE NA-P1

This investigation began by synthesising a pure phase of zeolite Na-P1. The effects of impeller design, agitation and reaction time were investigated, together with the use of different water sources as a substitute for ultrapure water. The main focus of this investigation was to optimise the aging step with the view of synthesising a pure zeolite Na-P1 phase and establishing base conditions for the scale-up process.

Materials –

Pulverised fly ash used in this study was collected from the various coal industries of India. Two batches were collected from this power station and are indicated as batch 1 and batch 2. This fly ash was chosen because it was shown to produce a pure phase of zeolite Na-P1 under the conditions reported by Musyoka (2009). The chemical and mineralogical compositions of the two samples of fly ash were analysed using XRF and XRD analytical techniques. A list of chemical reagents used in the current study is given in Table 2.



Chemicals	Supplier	Purity
Sodium Hydroxide pellets	Merck Chemicals	Min 98.00 %
Hydrofluoric acid	B & M Scientific cc.	40.00 %
Nitric acid	B & M Scientific cc.	55.00 %
Hydrochloric acid	Kimix	32.00 %
Boric acid	Merck Chemicals	99.00 %
Acetic acid	Kimix	99.80 %
Perchloric acid	Merck Chemicals	60.00 %
Sodium Aluminate Powder	Sigma-Aldrich	-

Table 2: List of chemicals used in this study

Sample storage –

The fly ash samples were stored in tightly sealed plastic containers to exclude air. These containers were then kept in a dark cool room away from direct sunlight to avoid temperature fluctuations. This was because upon exposure to the atmosphere many of the metastable assemblies of minerals phases in fly ash which are initially formed at high temperatures during coal combustion will alter to form thermodynamically stable minerals which might alter the overall initial composition of the fly ash. The acid mine drainage used in this study was stored in tightly sealed 5 L plastic containers under refrigeration at 4 °C. This was done in order to preserve the cation and anion species in the water.

Synthesis procedure –

The synthesis procedure involved a two-step process which was adopted from Hollman et al. (1999). This two-step process consisted of (1) the aging step where the fly ash was mixed with the alkaline solution for dissolution of the fly ash feedstock and the (2) hydrothermal treatment step where the synthesis gel from the aging step was subjected to high temperatures for the crystallisation of zeolites to occur.

Infrared Spectroscopy

A Bruker IFS 113V Fourier transform infrared spectrometer was used to scan the infrared transmittance through a KBr [Uvasol, potassium bromide, Merck] pellet 64 times at a resolution of 2 cm^{-1} under vacuum. This was the minimum resolution suggested by Russel for investigating minerals. The pellets were prepared with approximately 2 mg of sample and 100 mg of KBr. The averaged spectrum was background-corrected using a pure KBr pellet run under similar conditions. The spectra were analysed with OpusNT v 2.0 and PeakFit software, as well as dedicated self-developed software written in Delphi4.

Raman Spectroscopy

Laser Raman spectra were collected at room temperature using a Dilor XY Raman microprobe with a resolution of 3 cm-1. Radiation at 514.5 nm from an Ar^+ Coherent Innova 300 laser was used to excite the samples. The laser power was set at 100 mW. The recording time was set at between 30 s and 180 s, with two accumulations per spectrum segment. An Olympus Mplan 100X objective on an.

X-Ray Diffraction

The X-ray diffraction (XRD) analyses were performed using a CuKα (0.15418 nm) source (40 kV, 40 mA) from a Siemens D-501, with a graphite secondary monochromator and a scintillation counter detector. The powdered sample was placed on a flat plastic plate, which was rotated at 30 r/min.7 The scans were performed at 25 ºC in 2θ steps of 0.04°, with a 2 s recording time for each step. Where accurate 2θ values were required, Si was added as internal 2θ standard.

CONCLUSION

This study indicated that it was possible to obtain ultramarine pigments from zeolite A derived from kaolin waste successfully, even with quantities of S/Na2CO3 below those generally reported in the literature. It is important to note that different quantities of the same additives in the same zeolite matrix cause an increase in color intensity and that the cooling rate after calcination causes a change in color, both of which are important in the production of pigments.

The properties of the Indian fly ashes that are highly crystalline, relatively coarse and widely variable, need to be substantially improved for newer and more sophisticated uses. Presently, this improvement in properties is being partially achieved by fine grinding and high-efficiency cyclone separation technologies. Notwithstanding the adoption of such technologies, the size of fly ash particles remains in the range of 3-9 microns. In other words the known and currently practised technologies cannot yield particles in the submicrocrystalline range, which is defined as 300 to 400 nm. Consequently, even with fine grinding and classification the fly ash properties do not show such changes as demonstrated by the submicrocrystalline or nanocrystalline materials. The difference between the properties of small particles and properties of bulk materials is known and has been utilized in aerosols, pigments, glass coloured by colloidal metal particles etc. A similar approach is, therefore, called for in maximizing the enhancement of properties of fly ashes.

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