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AN ANALYSIS UPON CHARACTERIZATION OF FLY ASH AND ULTRAMARINE PIGMENTS

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An Analysis upon Characterization of Fly Ash and Ultramarine Pigments

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Abstract – This paper for the first time reports the conversion of coal fly ash into intense blue ultramarine via thiocyanate aluminosilicatesodalite $Na_8[AlSiO_4]_6(SCN)_2$. The possibility of stepwise and systemic conversion of thiocyanate aluminosilicatesodalite into intense blue ultramarine had never been previously demonstrated. The ultramarine analogs of various colors have been prepared by structure conversion of thiocyanate aluminosilicatesodalite by calcinations (500–950°C). The products obtained are characterized by various investigative techniques including Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, X-ray diffraction (XRD), UV visible spectroscopy, scanning electron microscopy (SEM), electron spin resonance (ESR) spectroscopy. Surface morphology is studied by the SEM technique. These extensive characterizations showed that the ultramarine pigment is good enough and that the sodalite framework is thermally highly stable with its structure undisturbed even at 950°C.

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FLY ASH : THE CONCEPT

Fly ash is a by-result of the combustion of pulverized coal in thermal power plants. The dust-accumulation system expels the fly ash, as a fine particulate deposit, from the combustion gasses before they are released into the air.

Fly ash particles are regularly round, running in distance across from\1 lm up to 150 lm. The kind of dust accumulation hardware utilized to a great extent decides the scope of particle sizes in any given fly ash. The fly ash from boilers at some more seasoned plants utilizing mechanical gatherers alone is coarser than from plants utilizing electrostatic precipitators.

The sorts and relative amounts of incombustible matter in the coal utilized decide the chemical composition of fly ash. More than 85 % of most fly ashes include chemical mixes and glasses framed from the components silicon, aluminum, iron, calcium, and magnesium. For the most part, fly ash from the combustion of subbituminous coals contains more calcium and less iron than fly ash from bituminous coal. Unburned coal gathers with the fly ash carbon particles, the amount of which is determined by such elements as the rate of combustion, the air/fuel, and the level of pummeling of the coal. When all is said in done, fly ash from subbituminous coals contains next to no unburned carbon. Plants that work just discontinuously (top burden stations), burning bituminous coals, deliver the biggest rate of unburned carbon.

The term fly ash was initially utilized as a part of the electrical power industry ca. 1930, the principal far reaching information on its utilization in concrete in North America were accounted for in 1937 by Davis et al.. The primary major viable application was accounted for in 1948 with the production by the United States Bureau of Reclamation if information on the utilization of fly ash in the development of the Hungry Horse Dam. Overall acknowledgment of fly ash slowly followed these early endeavors, however intrigue has been especially recognizable in the wake of the quick increment in vitality costs (and consequently cement costs) that happened amid the 1970s.

Fly ash is a fine-grained material comprising generally of round particles. A few ashes likewise contain unpredictable of precise particles. The size of particles changes relying upon the sources. A few ashes might be better or coarser than Portland cement particles. Figures 1 and 2 demonstrate the scanning electron magnifying lens (SEM) micrographs of cleaned segments of subbituminous and lignite fly ashes. Figure 3 demonstrates an auxiliary electron SEM picture of bituminous fly ash particles.

Some of these particles seem, by all accounts, to be solid, though some bigger particles seem, by all accounts, to be segments of thin, hollow circles containing numerous littler particles. Dry-and wet-sieving methods are usually utilized as a part of the estimation of fineness of fly ashes. ASTM assignment

C311-77 prescribes deciding the amount of the sample held when wet sieved on a 45 lm sifter, as per ASTM method C 430, with the exception of that a delegate sample of the fly ash of natural pozzolan is substituted for pressure driven cement in the determination. Dry sieving on a 45 lm strainer can be performed by method set up at CANMET. A few nations determine models for greatest deposit (in rate) held on a 45 lm strainer as follows.

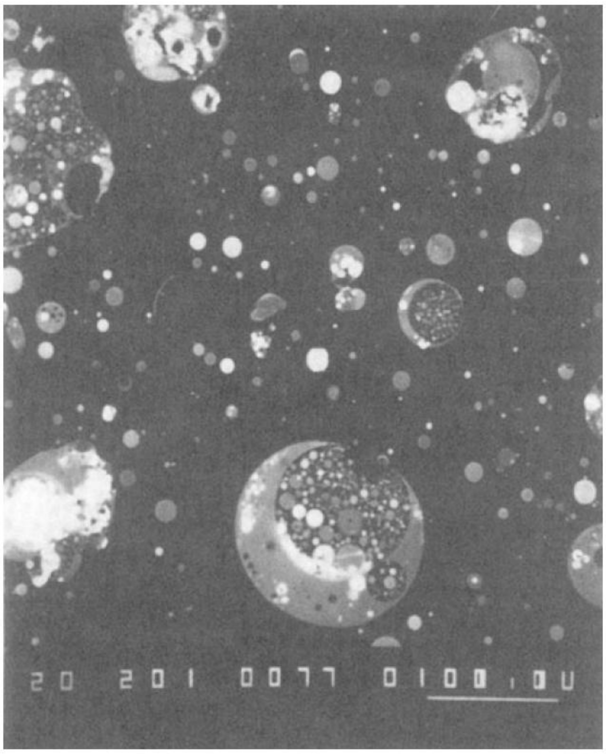


Fig. 1 SEM micrograph of a subbituminous ash (Backscattered electron image of a polished section of the dispersed sample)

Results of SEM and particle-size analysis have demonstrated that circular and adjusted fly ashes fluctuate in size from 1.0 to 150 lm fly ashes of unpredictable and precise shape are normally bigger.

Particle-size conveyance of fly ash can be determined by different means, for example, X-ray micrograph, laser particle-size analyzer, and coulter counter. Now and again, the agglomeration of various little particles may frame an expansive particle.

Much of the time, fly ashes contain particles of[1 lm breadth. Mehta (2004), utilizing a X-ray sedimentation technique, reported particle-size conveyance information for a few U.S. fly ashes. Mehta found that high-calcium fly ashes were better than the lowcalcium fly ashes, and he related this distinction to the nearness of bigger amounts of soluble base sulfates in high-calcium fly ashes.

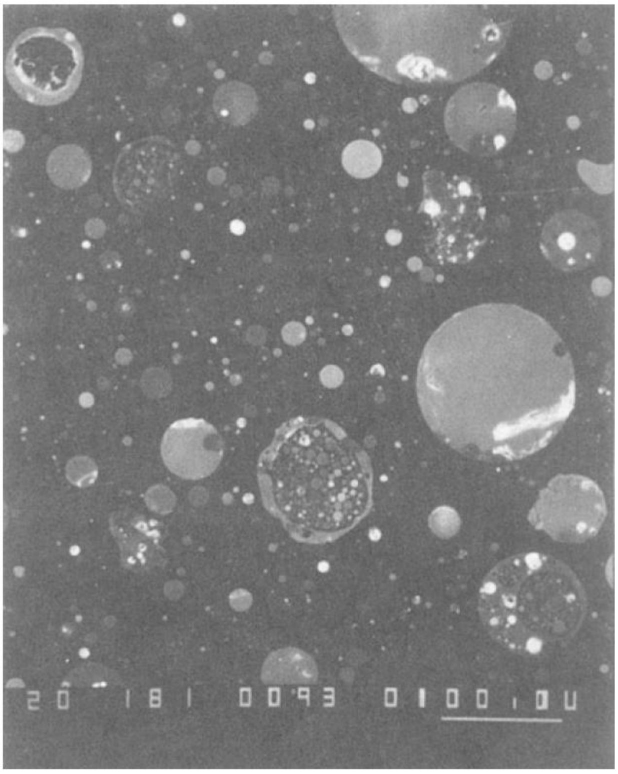


Fig. 2 SEM micrograph of a lignite fly ash (Backscattered electron image of a polished section of the dispersed sample)

The particular surface territory of fly ash, which is the region of a unit of mass, is quantifiable by different technique, which measures the resistance of compacted particles to a wind stream. ASTM C 204 depicts this method for the estimation of the surface range of Portland cement.

Particle-size analysis can likewise be utilized for the determination of the particular surface territory of fly ash; a laser particle-size analyzer is normally utilized for the estimation. The Brunauer–Emmett–Teller (BET) nitrogen ingestion technique has likewise been utilized for deciding the particular surface of the particles, however the results got by this method are generally higher than the results got by the Blaine particular surface-territory technique or particle-size analysis.

Cabrera et al. (2002) utilizing the Blain technique, particle-size analysis, and the BEST technique, measured and computed the particular surface zone of different fly ashes.

The particular surface qualities measured by the BEST technique are higher than the qualities got with the Blaine technique and particle-size analysis. This vast distinction is because of the face that BET technique measures the totality of voids in the surface of particles.

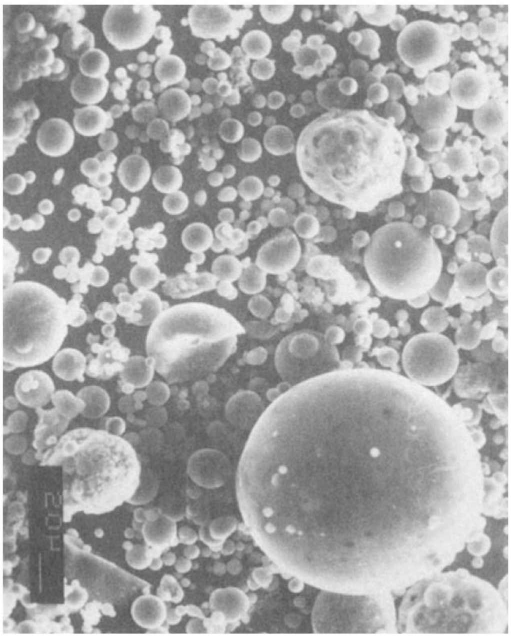


Fig. 3 SEM micrograph of a bituminous ash (Secondary electron image of the sample)

In general, both the sort and source of fly ash impact its mineralogical composition. Attributable to the fast cooling of smoldered coal in the power plant, fly ashes comprise of non-crystalline particle (B90 %), or glass, and a little amount of crystalline material. Contingent upon the system of burning, some unburned coal might be gathered with ash particles.

The X-ray diffraction (XRD) and infrared spectroscopy techniques are typically utilized for the determination of crystalline phases in fly ashes. The glass phases are determined by the low-edge XRD technique.

Notwithstanding significant amount of glassy material, every fly ash may contain one or a greater amount of the four noteworthy crystalline phase: quartz, mullite, magnetite, and hematite. In subbituminous fly ashes, the crystalline phases may incorporate C3A, C4A, S, calcium sulfate, and soluble base sulfates.

As was seen with chemical composition, the mineralogical composition of fly ashes via Carrette and Malhotra (2006) shifted over a wide range. Figure 4 appears a X-ray diffractogram for one of the bituminous fly ashes. A quantitative determination of the major crystalline phase contained in the fly ashes was additionally made by a quantitative XRD technique. The results are given in Table 1.

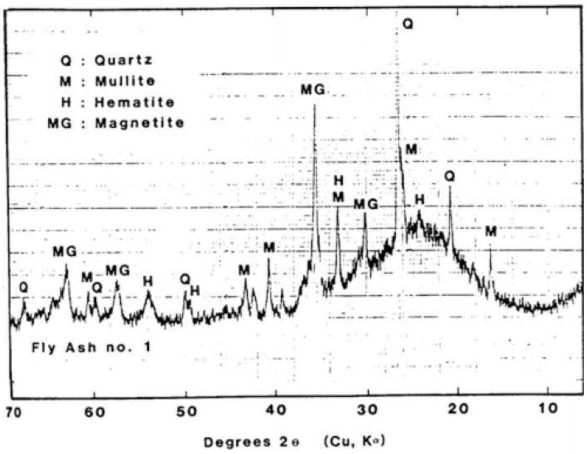


Fig. 4 X-ray diffractogram for a bituminous fly ash

Fly ash source	Type of coal[a]	Phase composition (%)					
		Glass	Quartz	Mullite	Magnetite	Hematite	LOI (%)
1	B	72.1	4.0	12.6	6.2	1.6	3.5
4	B	70.1	3.2	3.3	17.2	4.7	1.5
5	B	55.6	6.2	19.8	5.6	3.1	9.7
6	B	54.2	8.3	23.5	4.4	2.1	7.5
7	SB	90.2	2.9	6.1	–	–	0.8
8	SB	83.9	4.1	10.2	–	1.4	0.4
9	SB	79.8	8.7	11.5	–	–	0.8
10	L	94.5	4.6	–	–	–	0.9

Table 1 Mineralogical composition of some selected fly ashes.

ULTRAMARINE PIGMENT

Ultramarine is a natural pigment which has been used as a pigment since the middle ages. This inorganic pigment is a lazurite mineral extracted from the lapis lazuli rocks and is very expensive because of the complexity of the extracting process (Pascualet al., 2008). The applications of ultramarine are diverse and include the production of plastics, paints and powder coatings, printing inks, paper and paper coatings, rubber and thermoplastic elastomers, latex products, detergents, cosmetics and soaps, artists' colors, toys and educational equipment, leather finishes, powder markers, roofing granules, synthetic fibers, theatrical paints and blue mattes, cattle salt licks and white enhancer.

The industrial procedure for ultramarine fabrication was developed in France and Germany in 1828 (Sancho et al., 2008). Different formulations for the synthesis of ultramarine can be found in the bibliography. Studies show the following composition range for the synthesis of ultramarine: Na: 6.3-10, Al: 4.8-6, Si: 6-7.2, O: 24 and S: 1-4.5.

The structure and nature of ultramarine has been studied by different researchers. Ultramarine has the sodalite structure, consisting of b-cages in which different cations such as Ca2þ, Kþand Naþas well as anions such as OH_2,Cl_2, SO42 and Sn_2or even neutral water molecules can be entrapped (Kowalaket al., 2006). When Naþis present, the general composition is Na8-Y[Al62YSi6þ YO24Sx). The chromophors in this structure are believed to be radicals S22, S32 and S42, which result in colors of yellow, blue and red, respectively,. Color characterization of ultramarine was investigated by CIELab.

Kaolin, feldspar, sodium hydroxide, sulfur and a reducing agent such as charcoal have been used as themain component for the synthesis of ultramarine pigment. Some researchers have replaced kaolin with other materials such as zeolite and fly ash.

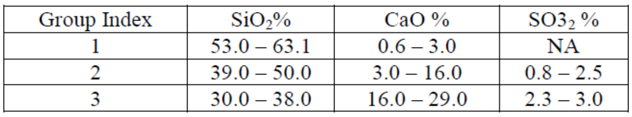
In this research, for the first time, nano-clay was substituted for kaolin, assuming that higher reactivity of nano-clay results in better colors.

Ultramarine has been for centuries one of the most highly prized pigments of all traditional artists' materials due to its durability, excellent colour, and its intrinsic value. It is made from the mineral lapis lazuli and although archaeological evidence shows that this mineral was used as a semi-precious stone and decorative building
stone from early Egyptian times, the earliest occurrence of lapis lazuli used as a painting was in sixth- and seventh-century AD wall paintings in cave temples at Bamiyan in Afghanistan, not far from the most famous source of the mineral. In Europe, the pigment probably found its most extensive use in the fourteenth to mid-fifteenth centuries, particularly in illuminated manuscripts and in Italian panel paintings. Because of its high quality and most intense blue colour, ultramarine can often be seen to have been reserved for the robes of Christ and the Virgin. In the late sixteenth and the seventeenth century, it has been noted that there was a shortage of the other most valuable blue pigment, azurite, which must have resulted in increased demand for that already costly ultramarine, thus making it even more precious and expensive. Since the price of this extraordinary pigment was sometimes even higher than that of gold, the motivation for producing a synthetic version accelerated the quest for a more favourably-priced substitute and the first synthetic manufacturing of the ultramarine pigment succeeded in 1828[1]. Because of their almost ten times lower price, they are being widely used in nearly all of the art works today, even though some critics claim they are less pure and less permanent then the pigment obtained from lapis lazuli.

FLY ASHES AND THEIR CHARACTERISTICS - MECHANO-CHEMICAL ACTIVATION

The Indian low-lime fly ashes are portrayed by moderately higher centralization of SiO_2 and Al_2O_3 and lower substance of Fe_2O_3. This suggests higher combination temperature for these fly ashes and, therefore, the odds of lower glass development, if the ash is not subjected to moderately high temperature. While in the low-calcium fly ashes the silica substance is twofold of the alumina content, in the high-calcium fly ashes the substance of these two oxides is all things considered similar or near each other. The iron oxide setting in the high-lime fly ash is essentially higher than in the low-lime assortment. Ponders including sieving, sink-skim and attractive separation, did to contemplate the heterogeneity of fly ashes, uncovered that the variability of composition is more in the high-lime fly ashes [Das 2003].

A study has been directed to classify the oxide compositions of fly ashes utilizing outspread premise capacity neural system [Nataraj et al 2006]. The following three primary gatherings of fly ashes have been recognized from around 80 sets of information :



Group Index	SiO_2%	CaO %	$SO3_2$ %
1	53.0 – 63.1	0.6 – 3.0	NA
2	39.0 – 50.0	3.0 – 16.0	0.8 – 2.5
3	30.0 – 38.0	16.0 – 29.0	2.3 – 3.0

Group Index 1 relates to the proper pozzolanic variety with little or no cementitious properties while the Group Index 2 and 3 cover fly ashes with cementitious properties with progressively increasing heat of hydration.

It is broadly realized that the reactivity of fly ashes is subject to their glass content and other mineral phases present. It has been watched that the Indian fly ashes are more crystalline than those acquired in different nations, the glass content extending from 47.0 to 60.9 for every penny (Fournier et al 2004). The system hypothesis of glass development gives a hypothetical premise to clarify the moderately poorer glass content in the Indian fly ashes. Since the proportion of system formers (SiO_2 + Al_2O_3 + Fe_2O_3) to network modifiers (Na_2O + K_2O + CaO + MgO) in the Indian fly ashes is high and imbalanced, the glass substance is low. Nevertheless, the fly ashes contain circular hollow particles (cenospheres), epitomized hollow particles (plerospheres), rakish glass pieces and crystalline grains in shifting extents as appeared in Figure 5.

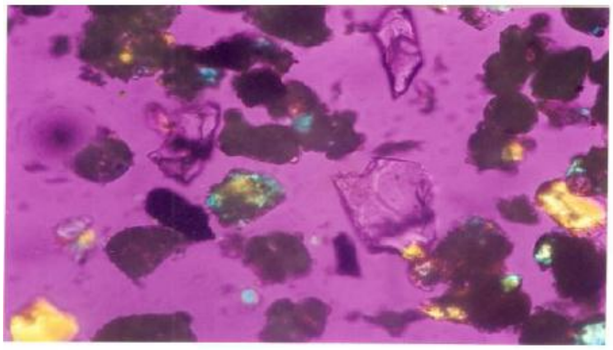
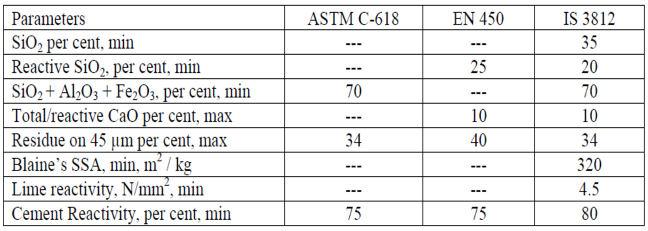


Fig.5.Fly Ash Particles in Low Magnification (x200) Showing Angular Glass Fragments

The present utilization of fly ash in the cement industry alone is assessed at more than 25 million tons for every year on the presumption that the creation of Portland Pozzolana Cement is more than 100 million tons for each year with fuse of no less than 25 for every penny fly ash per ton of cement delivered. In the event that the ingestion of fly ash can be improved everywhere throughout the industry to the present reasonable breaking point of 35 for each penny, the utilization of fly ash in the cement industry alone may ascend to around 60 million tons for each year by the year 2011-12. The acknowledgment of this vast potential is needy, to a huge degree, on improving the pozzolanicity or reactivity of fly ash by embracing more current beneficiation advancements. It is to some degree dicey if the present standard detail of fly ash (Table 2) would be satisfactory to accomplish the above target.



Parameters	ASTM C-618	EN 450	IS 3812
SiO_2 per cent, min	---	---	35
Reactive SiO_2, per cent, min	---	25	20
$SiO_2 + Al_2O_3 + Fe_2O_3$, per cent, min	70	---	70
Total/reactive CaO per cent, max	---	10	10
Residue on 45 µm per cent, max	34	40	34
Blaine's SSA, min, m^2 / kg	---	---	320
Lime reactivity, N/mm^2, min	---	---	4.5
Cement Reactivity, per cent, min	75	75	80

Table 2 Specification of the Indian Low-lime Fly Ash vis-à-vis the US and European Standards.

Endeavors so far have been to set up the reasonableness of the Indian cement and fly ashes to meet the item prerequisites and to build concrete asphalts on trial premise [Desai 2006]. The present confinements of the Indian Codal arrangements are additionally being inspected. From the studies did it creates the impression that with high-quality cements with 28 days compressive quality of more than 53 N/mm2 and fly ash of high reactivity as reflected through their lime reactivity (>6.0 N/mm^2) and cement reactivities (>90%), one may accomplish upto 70% replacement of cement in HVFAC, utilizing SNF based superplasticisers.

It is currently genuinely surely understood that a basic liquid could be utilized to respond with the silicon and aluminum in a source material of geographical birthplace or in by-item materials, for example, slag or fly ash to create folios. Since these reactions speak to an inorganic polymerization handle, the phrasing begat was "geopolymer". The polymerization procedure includes a significantly quick chemical response under soluble conditions on Si-Al minerals that result in a three-dimensional polymeric chain and ring structure comprising of Si-O-Al-O bonds. Low-calcium fly ash has been effectively used to fabricate geopolymer concrete, when the silica and alumina constitutes around 80% by mass with Si-to-Al proportion of around 2. The substance of iron oxide more often than not went from 10 to 20% by mass, while the calcium oxide substance was under 3% by mass. The carbon setting of the fly ash as determined by the misfortune on ignition, was under 2%. The composed particle size appropriation was observed to be 80% particles to be below 50µm [Rangan 2007].

The reactivity's of fly ashes concerning the geopolymeric items have been assessed with the assistance of a pseudo-ternary composition outline appeared in Figure 6.. From Figure 6 unmistakably ashes with low system modifier content tend to deliver poor salt initiation items, with quality by and large expanding as a component of system modifier content for low-lime fly ashes.

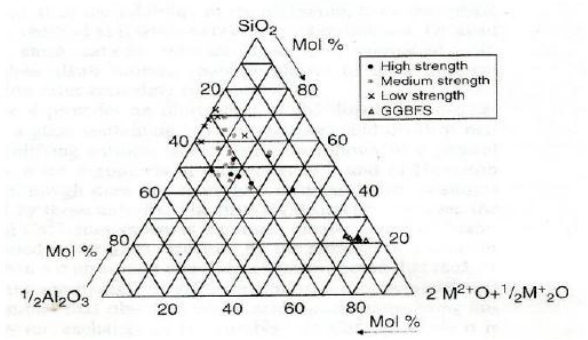


Fig. 6. Pseudo-Ternary Composition Diagram for Fly Ashes

The perception that system modifier substance is a pointer of the potential failure of a given fly ash in geopolymerization clearly conveys consideration regarding the utilization of high-lime or Class C fly ashes. It has been watched that in addition to the fact that it is conceivable to use Class C fly ash in geopolymers however in reality it can be to a great extent ideal, if the rheology of the blend can be enough controlled. All in all it appears that glass chemistry and accessibility of aluminum to a huge degree control the properties of geopolymers.

Fly ash, limitedly, is utilized as a mineral filler as a part of plastics. The results of numerous trial concentrates on led with fly ash have demonstrated that the expansion of fly ash filler builds the solidness of a plastic plan, yet like most fillers, lessens the effect resistance. Be that as it may, the immaculateness and particle size are the most imperative prerequisites. Aside from polymers, fly ash is frequently considered as a filler for paints furthermore as an extender for veneers. At first sight reasonableness of as-got fly ashes for these sorts of utilizations is somewhat constrained. One of the most recent improvements is the utilization of fly ash in metal-matrix composites as appeared in Figure 7. [Withers, 2008].

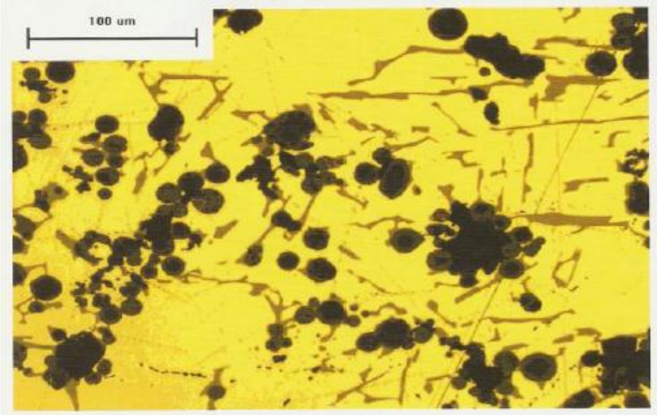


Fig. 7. Photomicrograph of Ultatite Composite showing Black fly Ash Spheres in Yellow Matrix of Aluminum.

SYNTHESIS OF ULTRAMARINE BLUE FROM WASTE COAL FLY ASH

Ultramarine is a natural blue pigment in view of the naturally happening mineral lapis lazuli. The principal utilization of lapis lazuli was accounted for in the 6th and seventh century in Afghanistani Zoroastrian caverns. It is an intricate blend of limestone, silicate minerals and pyrite containing minerals. Ultramarine is highly prized for its extreme dark blue color and for its high thermal solidness. Since naturally happening lazurite contains metal oxides and sulfide debasements, it is hard to separate immaculate ultramarine. Syntheticmethods for planning of ultramarine blue by Guimet in 1826 and Gmelin in 1928 were created.

Ultramarine is one of the types of sodalite, containing S_2^- and S_3^- radical ions, which are responsible for its color. Both radical ions are present in ultramarine blue, with the percentage of S^-_3 comparably greater. A typical sodalite cage structure is shown in Figure 8.

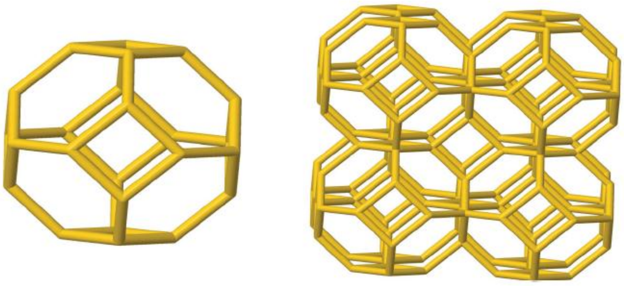


Figure 8. Unit cell of sodalite cage and sodalite crystal structure.

The ultramarine pigments are aluminosilicatesodalite structures containing sulfur chromophoric having general formula $Na_8[AlSiO_4]_6(S_2\ \ S_3)_2$. A few researchers have suggested different compositions of ultramarine blue pigments including, $Na_7Al_6Si_6O_{24}S_3$ and $Na_{6-10}Al_6Si_6O_{24}S_{2-4}$. Its synthesis involves the aluminosilicate source as a kaolin, sulfur, sodium carbonate, and reductive agents (charcoal, tar, etc.) at high temperature (800–900°C) for a long time. Both natural and synthetic ultramarine exhibit the sodalite structure and the chromophore sulfides (mostly NaS_3 and NaS_2) encapsulated in the β-cages are responsible for the blue colour. Ultramarine and its analogs are synthesized from different starting materials including Kaolin, zeolites, and fly ash.

Reports that are accessible in the literature demonstrate that the majority of the ultramarines are synthesized by utilizing sodium polysulfide and sulfur calcined in a nitrogen environment. Artist et al. (2014) made an endeavor to synthesize ultramarine utilizing zeolites as beginning materials.

The ultramarine that were acquired had a slight blue coloration, were unsteady, and were never a genuine ultramarine blue.

As needs be, the present work was started with the motivation behind figuring out if it was conceivable to make a ultramarine blue with awesome chromatic power from manufactured sodalite. It was additionally attractive to build up a procedure which was not just more fit for logical control than different methods but would likewise create a beneficial color in a shorter time interim than the one-to two-week term required by utilizing waste coal fly ash as a beginning material.

Reports accessible in the writing uncover that most of the ultramarines are synthesized by multistep forms utilizing Kaoline, sulfur, sodium, carbonate, and diminishing operators. Now and again chromophores of ultramarine pigments, in which sulfur was joined into pens as a sodium salt, were gotten. Weller et al. recommended that little colorless sulfur species diffuse into sodalite to forman middle of the road ultramarine.

The greater part of the methods accessible require elaborate mechanical assembly and controlled conditions. Subsequently, the present work intends to examine a basic method to synthesize ultramarine utilizing coal fly ash by utilizing hydrothermal and after that a structure transformation method.

Sodalite synthesis - Coal fly ash collected from thermal power station, Eklahara (Maharashtra, India), was fused with sodium hydroxide at 550°C for two hours. A stoichiometric mixture of fused mass obtained after the fusion process (containing sodium salts of silicates and aluminates) and sodium thiocyanate was then mixed together in a Teflon container in an aqueous medium. The mixture was then shaken vigorously for few minutes and kept in the oven at 100°C for six days. After completion of the reaction the white product was filtered and dried at 100°C overnight. This synthesized sodalite was characterized and subjected to thermal treatment in the temperature range of 400–950°C. At high temperature (950°C), the sodalite framework remains unaltered but beautiful intense blue ultramarine is generated.

Characterization - Coal fly ash and synthesized pure aluminosilicate thiocyanate sodalite and thermally treated ultramarine blue were characterized by various analytical techniques. IR absorption analysis (KBr disc technique) was performed on a Shimadzu, IRAffinity spectrometer in the range of 4000–400 cm−1 by transmission experiments and spectra were analyzed by using IR Solution software.

To obtain crystalline phases of the materials, the samples were examined by Philips PW-1710 operating at 25 kV and 25mA using Cu-K*α* radiation with wavelength *λ* = 1.54 Å.

Ultraviolet spectra were recorded by Shimadzu UV2450 instrument equipped with DRS accessories using barium sulfate as standard. Spectral data were collected in the range of 200–800 nm. Raman spectra were recorded by a Laser Raman WD Almega XR (Thermo-Nicolet) at room temperature. The instrument was equipped with a CCD Detector and a532 Ar (Green) LASER with a maximum power of 25mWand with an acquisition time of 30 s.

Scanning electron microscopy (SEM) was carried out to provide information about the surface morphology and crystal growth mechanism. The SEM was recorded on a JEOL JEM-6360A model equipped with a JEOL JEC 560 auto carbon coater. Electron spin resonance experiments were carried out at room temperature.

ULTRAMARINE BLUE FROM ASTURIAN “HARD” KAOLINS

The historical backdrop of ultramarine blue does a reversal to Bible times, being still utilized generally today. The natural material with the common color is the mineral lazurite or lapis lazuli. The old exchange of these stones from Afghanistan offers ascend to the name of the powdered stone, utilized for canvases and decoration, ultramarine blue (UB in the following), as a result of the long outing from abroad of this acknowledged material. This colored mineral achieved a high cost because of its lack, and toward the start of the nineteenth century UB was synthesized as a result of the huge interest.

China earth kaolin has been the customary raw material for UB pigment engineered generation. Then again Asturian stone earth (kaolin) has been utilized for a long time in the generation of obstinate material, essentially when the basic and iron substance allows coming to a suitable estimation of unmanageability. The more particular needs of materials for steel headstrong creation made the Asturian kaolin business diminish a considerable amount. This prompted the halting of the vast majority of the makers, in light of the fact that no one of them had introduced a refinery, despite the fact that exploration clarified the business enthusiasm of refining Asturian hard kaolin stores. The focus studies and research opened up the likelihood of the utilization of the kaolin delivered, even not being plastic, for different purposes where the kaolin has significantly more esteem included. Some physical cleaning and the particular hydrometallurgical treatment produce white kaolin, fascinating for paper filler and ceramics.

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	L. on I.
Asturian	49	37	0.35	0.9	0.10	0.03	0.50	0.10	12.02
China	48.5	38	1.1	0.03	0.10	0.30	1.85	0.10	10.02

Table 3 : Chemical composition of kaolins, wt.%

This study deals with the use of Asturian kaolin for UB pigment synthesis in comparison with China clay kaolin from Devon.

Industrial procedure for UB fabrication was developed by J.B Guimet in Toulouse (France) and C. Gmelin in Germany 1828. F.A. Köttig improved the process for the Royal Porcelain Manufacturing (Mertens, 2004).

Different UB formulations can be found in the bibliography (Gobeltz-Hautecoeur et al., 2002) gave the following range composition: Na 6.3–10, Al 4.8–6, Si 6–7.2, O 24, S 1–4.5.

Structurally UB pigment has an aluminosilicate framework (sodalite type) with Na+, S2−, S3− and SO4 = ions inside (Arieli et al., 2004). S3− polisulphur radical produces the strong blue colour as could be deduced from most references that attribute to S3− chromophore the blue colour of the UB. For that, characterization of UB is done frequently determining the presence of this polyanion and quantifying it.

Sample	*T* (°C)	Light	*L*	*a*	*b*
China	700	N (natural)	34.5	18.5	−51.2
Asturian	750	N	37.5	15.0	−48.5
	700	N	38.5	14.0	−47.2
	680	N	35.5	18.5	−50.5
	650	N	37.5	17.3	−50.1

Table 4 Activation temperature determination by colour results.

The structure and nature of UB has been studied by different methods: XRD, NMR, RE, IRS, ESR, EPR. Colour characterization is made by the determination of the colorimetric parameters and making visible reflectance studies.

Some of the best representations of the UB crystal structure are described in the papers by Gobelts-

Hautecoeur et al. (2002), that include the S3− chromophore and four Na+ cations. This shows only three Na+ cations and the S3− chromophore polyion. A β-cage containing the ions, as well as the geometrics of S3−, S2− and (Na4S3)3+, with the interatomic distances, are described by Arieli et al. (2004). Not all the β-cages are filled with S3−, being possible the filled percentage determination.

Colorimetric studies of the pigment follows the indications defined by the Commission International d'Eclarage CIE (1976) as described in the works of Gobeltz and Kowalisky.

The Use of Ultramarine Pigments in Cosmetics The natural form of the mineral ultramarine blue is, lapis lazuli, but our discussion focuses upon the synthetic or artificial varieties of ultramarine pigments as used in the cosmetic and personal care industries.

CONCLUSION

A new method for synthesis of intense ultramarine blue was reported in this study. The presented results indicate that the colored products can be obtained from coal fly ash via aluminosilicate thiocyanate sodalite. The original structure of the aluminosilicate sodalite synthesized from coal fly ash remains unaltered during thermal treatment at 950°C and is confirmed by XRD data.

It has been observed that by reducing the mean particle size of the fly ashes from 30 μm to below 10 μm, substantial improvement in the flow and strength properties of mortars and concrete are achieved but the enhancement of properties corresponding to further reduction of fly ash particle size to even 3-5 μm is either incommensurate or inconsistent.

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.

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