CHAPTER -02

LITERATURE REVIEW

2.1 General

This chapter presented the comprehensive review of past study & analysis on the effective usage of Pond ash, Red mud, and MSW reject. The chapter also discusses the use of these industrial by-products in the process of geopolymerization process. It further explores the work of various researchers, sheds light on their investigations into the mechanisms underpinning geopolymer synthesis and its applicability in civil engineering as a substitute for traditional construction materials.

The chapter emphasizes both the mechanical (compressive) and mineralogical attributes of the developed geopolymers, supported by citations from research studies. In the end, it aims to highlight the overall significance of the current research and elucidate the existing gaps in the past research related to geopolymerisation.

2.2 Various Studies on Geopolymerization and its Mechanism

The increasing generation of industrial waste and the need to address disposal challenges and combat global warming have spurred researchers to develop synthetic materials. Among these materials, alkali-activated inorganic polymers, known as geopolymers, have emerged as valuable solutions for building and solidification applications (Wang et al., 2019). Geopolymerization is the fundamental process involving the mixing of aluminosilicate materials with an alkali solution, as detailed in studies by Wongsa et al. (2017) & Roviello et al. (2016). Deb et al. (2014) have documented that the substitution of Portland Cement (OPC) with a mix of slag and fly ash yields a significant lowering in CO_2 emissions. Leveraging supplementary industrial waste residues like ash from the combustion of coal, silica fume, metakaolin, slag (iron ore residue), and various other industrial waste materials in concrete applications and soil stabilization/solidification has proven advantageous (Chalee et al., 2013; Chalee et al., 2010 & Krammart et al., 2004) through the geopolymerization process.

During the 1970s, Professor Joseph introduced the term “Geopolymer.” Geopolymer denotes a composite material created by alkali-activating aluminosilicate substances under specific temperature and pressure conditions. This geopolymer is defined by the equation $M_n[-(SiO_2)-AlO_2]_n\ zH_2O$, where z can take values of 1, 2, or 3, M represents an alkali metal cation (such as K or Na), and n signifies the extent of polymerization reactions (Davidovits and Sawyer, 1985 & Davidovits, 2008).

The geopolymerization process encompasses four fundamental phases: Reacting with a highly concentrated alkaline activator. Dissolving oxides from the alumina-silicate-rich raw materials, facilitating the transition of dissolved oxide minerals, inducing coagulation and gelation, ultimately resulting in polycondensation and the development of a stable 3-D network of silicoaluminate structures (De Silva et al., 2007).

Davidovits (2011) reported in the study that a three-dimensional, amorphous polymer is formed by blending a strong aqueous solution of sodium hydroxide and sodium silicate with alumina-silica rich materials like slag, fly ash (PFA), metakaolin, and similar substances. This geopolymer technology has shown the potential to convert various industrial waste materials, including fly ash collected from power plants, GGBFS from steel and iron production, Red mud from alumina production, high-magnesium nickel slag, bottom ash from combustion of municipal solid waste, waste glass, dredged sediments, and discarded fired clay bricks, into valuable and usable products (Duxson et al., 2007; Okoye et al., 2017; Lirer et al., 2017; Saha and Rajasekaran, 2017; Kumar and Kumar, 2013; Zhang et al., 2017; Wongsa et al., 2017; El-Naggar and El-Dessouky, 2017 & Zawrah et al., 2016). Table 2.1 discussed the development of geopolymer from different industrial waste.

Geopolymer technology offers a promising solution for mitigating CO_2 emissions and reducing energy consumption associated with cement manufacturing. This is achieved through the conversion of industrial waste materials into usable, environmentally friendly alternatives (Zhang et al., 2017). In the recent decades, significant surveys have been directed towards the investigation of the reactions underlying the process of geopolymerization. The mechanistic process primarily involves the mixing of solid precursors enrich with aluminosilicate components and activator solution, typically an alkali hydroxide (such as NaOH or KOH) or alkali silicate (e.g., Na2O·nSiO2 or K2O·nSiO2) solution. Under highly alkaline conditions, the silicate and aluminate tetrahedral units are solubilized and commence polymerization or aggregation into oligomers as their concentration surpasses a critical threshold. These oligomers subsequently undergo further polymerization, resulting in the formation of amorphous network structures through covalent bonds that link silicate and aluminate tetrahedral. Alternatively, these are re-organizing as often resembling zeolites, particularly under hydrothermal conditions. These resulting geopolymers can be further transformed into crystalline structures through extended hydrothermal curing or high-temperature heating, a process known as calcination, in subsequent treatments. Zhuang et al. (2016) highlighted the geopolymer concrete that offers distinct advantages over ordinary Portland cement concrete, such as its notable properties of high early strength and enhanced resistance to chemical attack.

Table: 2.1 Synthesis of Geopolymer using Different Industrial Wastes

Author name	**Industrial waste**	**Curing period**	**Compressive strength**	**Alkaline activator**
Dassekpo et al. (2017)	Completely decomposed granite(CDG) , fly ash	Curing period of 7 Days	4.62-18.42 MPa	Sodium hydroxide and sodium silicate
Hanjitsuwan et al. (2017)	When Bottom ash replaced 30% calcium carbide residue (CCR) When bottom ash replaced with 30% Portland cement (PC)	At 28 days of curing period	11.4 MPa 13.8 MPa	Sodium hydroxide and sodium silicate
Duan et al.(2017)	Fly ash replaced with silica fume from 0 to 30%	At 28 days of curing period	90 MPa	Sodium hydroxide and sodium silicate
Blash and TVS (2016)	Fly ash and GGBS	At 28 days of curing period	69.43 MPa	Sodium hydroxide and sodium silicate
Allahverdi and Kani (2009)	Construction and demolition waste (C&D)	At 28 days of curing period	40 MPa	NaOH and Na_2SiO_3
Narayanan and Shanmugasundaram (2017)	Class F type fly ash having low calcium content	80^{o} C	27.20 MPa	Sodium hydroxide and sodium silicate and the ratio of SS/SH is 2.5
Wardhono et al. (2017)	Fly ash and GGBFS (Ground granulated blast furnace slag)	28 days to 540 days	22.2-32.2 MPa 39.5-40.4 MPa	Sodium silicate and sodium hydroxide

2.3 Factors Influence the Properties of Geopolymer

The reactivity of alumina-silicate sources depends upon a combination of factors, including their chemical composition, mineralogical and morphological structures, fineness, and the number of amorphous structures present, as elucidated by Tekin (2016)

2.3.1 Alkaline Activator

- The geopolymerization process relies heavily on the chemical or alkaline activators, as it plays a crucial role. Generally, a highly alkaline environment is necessary to promote the surface hydrolysis of the aluminosilicate particles in the raw material. Moreover, the concentration of the activator has a substantial influence on the material behaviour under load of geopolymers (De Vargas et al., 2011 & Hu et al., 2009).
- The dissolution of Si and Al species in the geopolymer synthesis process is greatly affected by the concentration of the chemical activator. The amount of Si and Al leaching is primarily governed by both the activator's concentration and the leaching duration (Panias et al., 2007).
- Gorhan and Kurklu (2013) in their study conducted a detailed investigation into the influence of chemical activator concentration. Their findings indicated that a low concentration of the activator does not sufficiently catalyse the geopolymer reaction, while an excessively high concentration leads to the premature coagulation of silica. In both scenarios, these conditions resulted in diminished strength of the geopolymer material.
- Ken et al. (2015) have reported the reduction in compressive strength with excessively increasing the concentration of the alkaline activator can be attributed to several factors: (a) the elevated viscosity of a sodium hydroxide solution, which is a consequence of its higher concentration, impedes the leaching of Si and Al ions. (b) High OH- concentration leads to the premature precipitation of geopolymeric gels. (c) Inadequate

dissolution of Si and Al species leads to partially reacted or unreacted raw material particles.

- The strongly alkaline solution, also known as the chemical activator, is essential for initiating the geopolymerization reaction, especially during the dissolution of silica and alumina species. Additionally, the chemical activator serves as a vital reactant in the poly-condensation reaction (Gorhan and Kurklu, 2014 & Khale and Chaudhary, 2007).
- An alkali solution is employed to dissolve alumina-silicates during the geopolymerization process, resulting in the formation of free silica and alumina tetrahedral units. Alkali metal cations act as charge-balancing ions, facilitating the linkage of SiO4 and AlO4 tetrahedral alternately. This linkage leads to the formation of polymeric precursors (-SiO4 - AlO4-, or - SiO4 - AlO4 -SiO4-, or - SiO4- AlO4 - SiO4 - SiO4 -) as oxygen atoms are shared between two tetrahedron units. This process ultimately produces monolithic geopolymer products (Kumar and Kumar, 2013).
- Numerous studies have demonstrated that the mixing of an alkaline solution generates a significant amount of heat. Therefore, it is recommended that the alkaline solution be left at room temperature for approximately 24 hours to reduce its temperature before mixing it with the dry mixture. However, some studies propose that the alkaline solution can be directly mixed with the dry mixture (Mehta and Siddique, 2017).
- Vora and Dave (2013) found that a higher compressive strength was attained when a mixture of sodium hydroxide and sodium silicate was employed, as opposed to using sodium hydroxide alone.

Mostly all researchers have employed a combination of sodium silicate and sodium hydroxide at particular ratio as the alkaline activator in geopolymer synthesis. Studies have shown that an elevation in the concentration of sodium hydroxide leads to increased compressive strength. This improvement in compressive strength is ascribed to the higher concentration of sodium hydroxide, which augments the solubility of aluminosilicate materials and fosters the geopolymerization reaction. Geopolymer compressive strength is subject to variations based on the alkaline activator-to-binder ratio. Researchers have noted that an increased alkaline activator to binder ratio leads to a decline in compressive strength. This drop in compressive strength is attributed to the higher alkaline activator to binder ratio causing an increase in water content (Hadi et al., 2017). An excess of OH- ions hinders the geopolymerization process, leading to a decrease in compressive strength. Sodium-based activators have demonstrated superior compressive strength at ambient temperatures compared to potassium-based activators (Hosan et al., 2016). The following Fig. 2.1 provides a comparison of the compressive strength between Na and K-based geopolymers. The K-based activator reported lower volumetric shrinkage and weight loss than the Na-based activator. Also, minimum surface cracks developed in the potassium-based geopolymer than the sodium-based geopolymer (Hosan et al., 2016). Geopolymer prepared with only sodium silicate solution reported higher compressive strength compared to the sample which developed with combined sodium silicate and sodium hydroxide solution (Huseien et al., 2016). The Table 2.2 represented the impact of ratio of sodium silicate (Na_2SiO_3) to sodium hydroxide (NaOH) ration on compressive strength of geopolymer.

Table: 2.2 Impact of Ratio of Na_2SiO_3 and NaOH on the mechanical property (compressive strength) of the geopolymer

Author name	**Ratio of sodium silicate/ sodium hydroxide**	**Ratio of alkaline activator/ binder mix**	**Compressive strength**
Zawrah et al. (2016)	2.5	0.30	83 MPa
Cheah et al. (2017)	1.2	0.11	49.61 MPa
Hadi et al. (2017)	Sodium hydroxide of 14M & NS/NH ratio (2.5)	0.35	The highest 7 day compressive strength is 60.4 MPa
Huseien et al. (2016)	Sodium hydroxide of 8M & NS/NH ratio (3.0)	0.30	56.4 MPa at ambient temperature 42.8 Mpa at elevated temperature
Sharmin et al. (2017)	2.5	0.5	The highest 47.85 MPa compressive strength with 14M for mix MK(25):RHA(25):GGBS(50)
Mermerdaş et al. (2017)	2.5	0.50	Optimized compressive strength for FA based and GGBS based light weight geopolymer are 10.767 MPa and 27.712 MPa
Narayanan and Shanmugasundaram (2017)	2.5	0.4	27.20 MPa highest compressive strength
Saha and Rajasekaran (2017)	1	0.4	The highest compressive strength 78.2 MPa

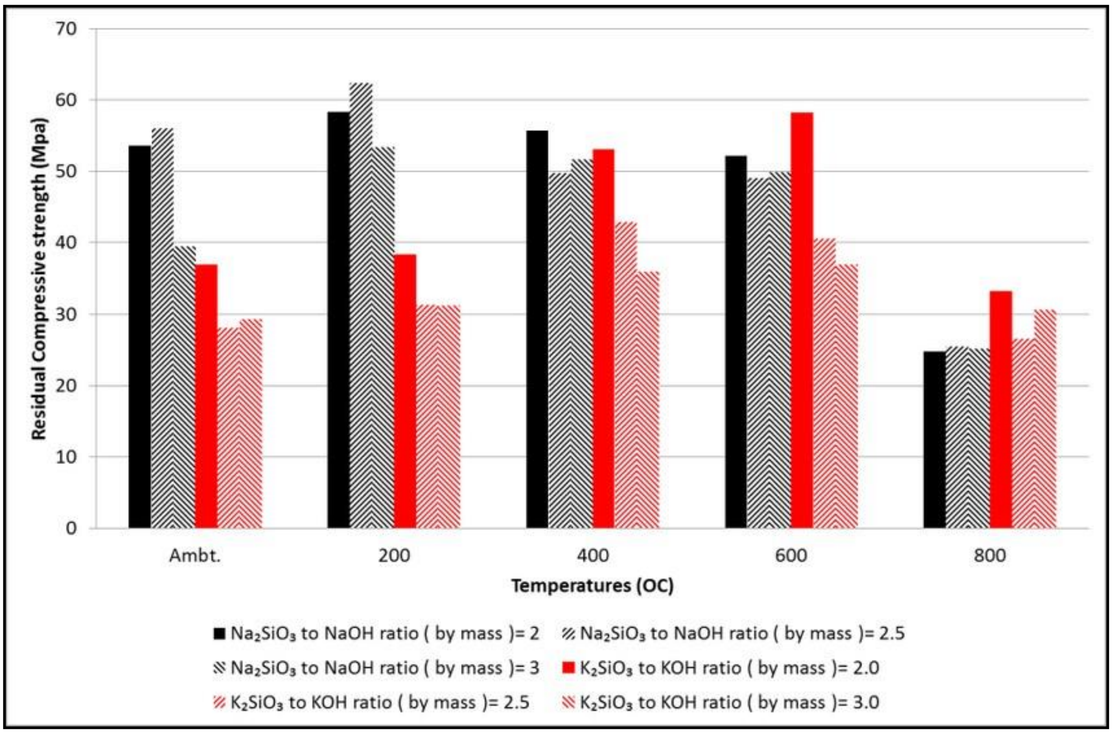

Fig: 2.1 Compressive Strength at different alkaline solutions (Hosan et al., 2016)

2.3.2 Composition of Raw waste material

- Hydration products depend upon the composition of the raw material. There are two types of hydrated alkali-activated materials (a) C-A-S-H geopolymeric gel, which serves as the primary reaction product in the high-calcium system involving GGBFS (ground granulated blast furnace slag) (b) N-A-S-H geopolymeric gel, which forms a three-dimensional network and is the predominant reaction product in the low-calcium system. (Huiskes et al., 2016)
- Sharmin et al. (2017) in their study determined that SiO2 and CaO in the base material played a significant role in enhancing the strength, while Al2O3 had an impact on the amorphous nature of the resulting products.
- The dissolution, hydrolysis and condensation reaction of geopolymers are greatly affected by the effective Si/Al ratio. In low Si/Al ratio geopolymer system the condensation reaction tends to occur between aluminate and silicate species, thus resulting in a mainly

poly (sialate) geopolymeric structure. On the other hand condensation reaction in a high Si/Al system would result in pre-dominantly between the silicate species itself, forming oligomeric silicate which in turn condenses with $Al(OH_4)^{4-}$ and form geopolymeric structures of poly (sialate-siloxo) and poly (sialate-disiloxo) (Weng & Sagoe-Crentsil, 2007; Sagoe-Crentsil & Weng, 2007).

- Arif et al. (2016) reported that sugarcane bagasse ash has been beneficial at a 5% replacement with cement due to pozzolanic and filler effect. But more than 5% replacement of cement with sugarcane bagasse ash, reduction has been observed in the pozzolanic activity. Due to having deactivate silica (α-quartz) rather than amorphous silica portlandite phase $Ca(OH)_2$ has been decreased.
- The physical properties, kinetic process and thermodynamic stability of resulting product affected by the percentage of the binder mix in the mixture which ultimately decide by the ratio of alkaline solution and binder mix.
- Materials with higher aluminium content in waste materials require a larger quantity of alkali solution to offset the negative charge originating from the tetrahedral AlO4 sites within the SiO4 framework. Also, the higher aluminium materials have a greater affinity to the water which results in a lower chemical bond (Ruiz-Santaquiteria et al., 2012).
- The materials which have high calcium content possess the C-A-S-H geopolymeric gel which assigns the vibration of asymmetrical stretching of bond (Si-O-Si or Si-O-Al) around at 960 cm^{-1} wavenumber. While on other hand the low calcium species developed the broader and asymmetrical vibration of bond (Si-O or Al-O) shifted towards the higher wavenumber (Garcia-Lodeiro et al., 2011). The following Fig. 2.2 clarifies the result between high calcium environment and low calcium material.

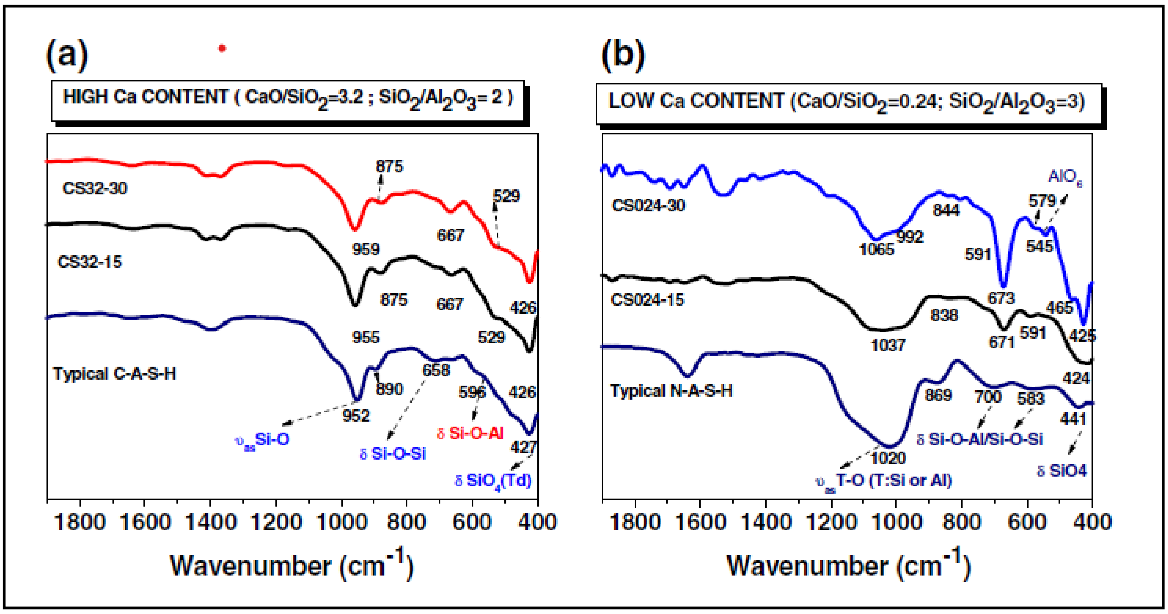

Fig: 2.2 Comparison of FTIR analyses between high Ca and low Ca content (Garcia-Lodeiro et al., 2011)

Table 2.3 represents the XRF analysis of various industrial wastes by various researchers **(**Zhang et al., 2017; Wongsa et al., 2017; EI-Naggar and EI-Dessouky, 2017; Lirer et al., 2017; Albitar et al., 2017; Hadi et al., 2017; Dassekpo et al., 2017; Nazari and Sanjayan, 2015; Lemougna et al., 2017; Chao-Lung et al., 2011; Castaldelli et al., 2016 & Zawrah et al., 2016; Murmu et al., 2019**)** that have been used for development of geopolymer. The composition of the above waste materials reported that these waste materials are full of aluminosilica sources which are necessary for the geopolymerization. However, variations in the oxides of silica, alumina and calcium affected the various parameters (compressive strength) of the composite geopolymer. The percentage of silica and alumina affects the geopolymer reaction.

Table: 2.3 (a) Composition of different waste materials by XRF Analysis reported by various researchers

Chemical composition	**Fly Ash**	**High magnesium nickel slag**	**MSWI Bottom Ash**	**Waste Glass**	**Dredged sediments**	**Granulated lead smelter slag**	**Ground granulated blast furnace slag**
SiO_2	53.0	52.3	15.8	82.52	44.17	27.5	32.40
Al_2O_3	30.6	6.2	0.9	3.18	14.18	7.4	14.96
Fe_2O_3	3.8	4.2	4.2	3.17	4.72	33.8	0.83
MgO	1.2	26.9	3.5	0.46	2.617	2.1	40.70
CaO	4.8	8.8	38.1	4.01	12.17	19.4	5.99
K_2O	1.4	0.2	7.3	1.15	3.84	….	0.29
Na_2O	0.5	0.1	0.2	3.65	4.70	….	0.42
TiO_2	1.1	0.1	0.3	0.50	0.50	….	0.84
LOI	2.3	0.5	23.0	0.41	….	…..	NA

Table: 2.3 (b) Composition of different waste materials by XRF Analysis reported by various researchers

Chemical composition	Completely decomposed granite	Aluminium slag	Grey cast iron slag	Red Mud	Ground Rice Husk Ash	Sugarcane Bagasse Ash	Waste fired clay bricks
SiO_2	40.35	8.35	63.6	9.39	91	43.34	50.16
Al_2O_3	30.41	60.8	2.68	18.47	0.35	10.45	15.95
Fe_2O_3	10.26	2.35	17.3	33.99	0.41	8.31	15.09
MgO	-	8.89	0.84	0.32	0.81	1.48	2.13
CaO	-	5.21	1.45	14.19		22.16	4.39
K_2O	1.36	0.80	0.31	0.10	3.21	2.18	1.48
Na_2O	0.18	2.75	2.08	5.11	0.08	0.19	2.43
TiO_2	1.00	0.12	0.59	5.42		2.88	2.10
LOI		1.99	1.68		8.5	7.61	2.10

2.3.3 Si/Al or SiO_2/Al_2O_3 Ratio

- Wan et al. (2017) carried out an extensive analysis to assess how the Si/Al ratio affects a wide range of geopolymer properties. Their findings revealed a discernible correlation between compressive strength and the Si/Al ratio. Remarkably, the greatest compressive strength was achieved when the silica /alumina ratio was 2:1. This peak strength level can be attributed to the optimal dissolution of silicon (Si) and aluminium (Al) precursors at this specific ratio, resulting in a harmonious acceleration of polymerization and condensation reactions. Importantly, the varying Si/Al ratios corresponded to distinctive structural configurations within the geopolymeric materials, as vividly depicted in Fig. 2.3.

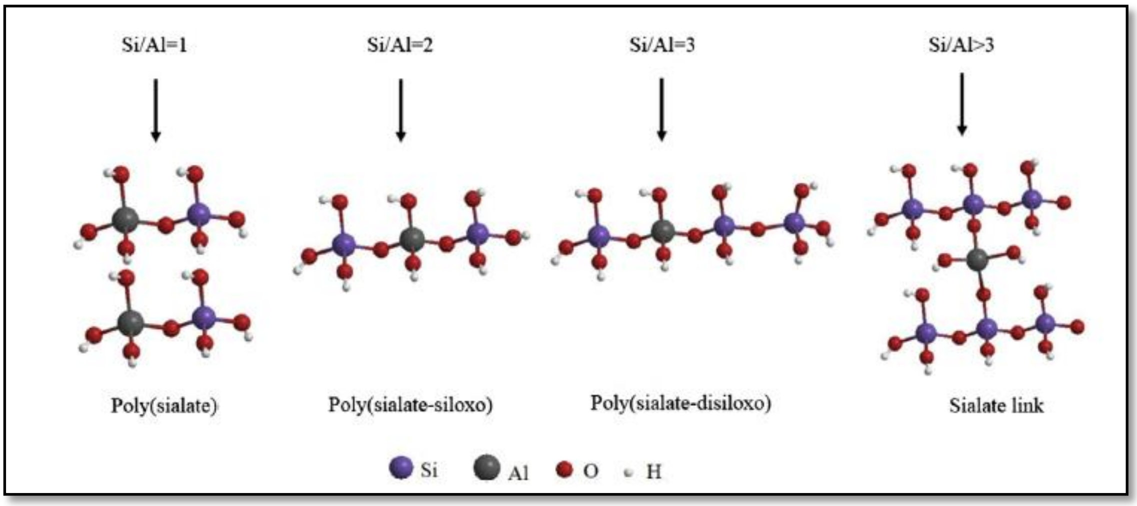

Fig: 2.3 Different bond structure of Geopolymer at Different Si/Al ratio (Wan et al. 2017)

- Bashar et al. (2016) observed that an increased SiO2/Al2O3 ratio significantly contributes to the improved compressive strength of geopolymer mortar. Additionally, as noted by Djobo et al. (2014) and Lampris et al. (2009), the introduction of a mineral-rich in soluble Al2O3, featuring an average particle size below 24.73 μm, offers the requisite quantity of amorphous aluminosilicate structure. This amorphous structure plays a pivotal role in facilitating the various stages of geopolymerization, including dissolution, nucleation, condensation, and reorganization of geopolymeric products.

- Najari and Sanjayan (2015) have demonstrated the feasibility of creating geopolymers utilizing aluminum and cast iron slag. Their work underscores the significance of the silica-to-alumina ($SiO2/Al2O3$) ratio as the paramount factor governing mechanical properties. It is well-established that specimens exhibit heightened compressive strength when a substantial $SiO2/Al2O3$ ratio is present in the initial paste, as corroborated by Komnitsas et al. (2015). An elevated $SiO2/Al2O3$ molar ratio promotes the creation of sturdy Si-O-Al and Si-O-Si bonds, leading to the formation of more compact and resilient geopolymeric structures.
- Conversely, when the $SiO2/Al2O3$ ratio is notably low, such as in the case of red mud paste at 1.33, the formation of aluminosilicate bonds is severely limited. Consequently, the ultimate strength of the geopolymer is also compromised, as observed by Duxson et al. (2005) and Leong et al. (2016).

2.3.4 Particle size of the material taken

- The granularity of the geopolymer source material greatly influences the extent of geopolymerization. Materials with larger particles and increased porosity typically display reduced reactivity, whereas geopolymer materials with finer particle sizes tend to attain a higher level of geopolymerization (Sathonsaowaphak et al., 2009; Chindaprasirt et al., 2009).
- Chindaprasirt et al. (2011) in their study undertook research on the production of high-strength geopolymer utilizing finely ground, high-calcium fly ash. They investigated how the fineness of fly ash affected various aspects, including the setting time of geopolymer paste, workability, strength development, and drying shrinkage in geopolymer mortars fabricated from finely classified, high-calcium fly ash. The

study’s findings indicated that with an increase in the fineness of fly ash, the setting time of the paste decreased. Additionally, the flow, strength, and drying shrinkage properties of the mortars demonstrated improvement when utilizing finer fly ash. It was noted that geopolymer mortars produced with coarser fly ash exhibited lower strength development compared to those made with finer fly ash (Fig 2.4 &2.5). Table 2.4 provides an overview of studies that examine the influence of particle size on the compressive strength of geopolymers.

Fig: 2.4 Scanning electron microscope (SEM) micrographs of fly ashes: Coarsed fly ash, Medium fly ash, Fine fly ash (Chindaprasirt et al., 2011)

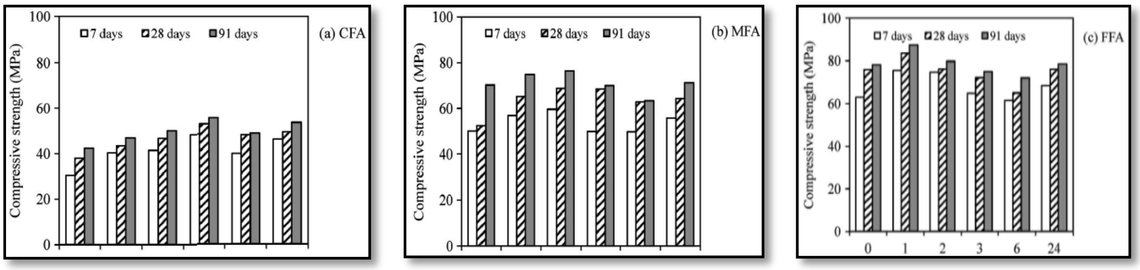

Fig: 2.5 Compressive strength of CFA, MFA and FFA geopolymer with days (Chindaprasirt et al., 2011)

Table: 2.4 Influence of particle size on the properties of geopolymers discussed by researchers

Sr no.	**Type of geopolymer**	**Fineness (Particle size)**	**Mechanical (Compressive) strength**	**Primary findings**
01	CDW (constructional demolition waste based geopolymer Vasquez et al.(2016)	CDW : 24.73µm, OPC: 21.65 µm, MK : 7.76 µm	17.5 (at 30% OPC at 28days) & 9.5 (at 10% MK at 28 days)	Addition of OPC is optimum
02	Bottom ash based geopolymer Hanjitsuwan et al.(2017)	BA: 2.12µm and 32.3µm CCR : 2.25 µm and 21.2 µm PC: 3.15 µm and 14.6 µm	13.8 MPa (at 30% PC) and 11.4 MPa (at 30% CCR) with bottom ash	Addition of Portland cement is optimum
03	Fly ash and silica fume based geopolymer Duan et al.(2017)	Fly ash : D_{90}-5.33 µm D_{50}-1.46 µm D_{10}-0.38 µm Silica fume : D_{90}-0.15 µm D_{50}-0.09 µm D_{10}-0.02 µm	90 MPa at 28 days (at 30% silica fume)	30 % silica fume gives higher compressive strength

2.3.5 Calcium additives

- Phetchuay et al. (2014) conducted a study that involved an investigation into the use of calcium carbide residue (CCR), a waste byproduct originating from acetylene gas industries, as an alkaline activator to improve the stabilization of problematic clay. Kamei et al. (2013) elucidated the influence of elevated bassanite content, a derivative of gypsum plasterboard waste, on the water content and dry unit weight of soil mixtures. This effect can be attributed to the inherent property of bassanite, a hemi-hydrate calcium sulfate ($\mathrm{CaSO4\cdot 1/2H2O}$), which exhibits a remarkable affinity for moisture in moist clay soil. This affinity leads to the conversion of bassanite into hydrated calcium sulfate ($\mathrm{CaSO4\cdot 2H2O}$), thus facilitating the recovery of a significant portion of water molecules.
- Mehta and Siddique (2017) examined the impact of varying proportions of added calcium content on gel formation. Furthermore, Latifi et al. (2016) conducted a micro-level investigation, revealing that calcium-based additives effectively reshaped the porous network within stabilized clays. This modification included the introduction of cementitious materials, such as calcium silicate hydrate (C-S-H) for montmorillonite clays and calcium aluminate hydrate (C-A-H) for kaolinitic clays. As a result, the structural integrity of the material was significantly improved. Table 2.5 represents the calcium-based additives that influence the geopolymeric reactions reported by researhers.

Table: 2.5 Chemical Compositions of Calcium-based Additives

Constituents	**CCR (calcium carbide residue)**	**High calcium wood ash**	**Phosphogypsum**	**Recycled bassanite**	**SH-85 (calcium additive)**
CaO	70.78	61.00	32.83	38. 63	68.20
SiO_2	6.49	2.70	12.87	-	9.25
Al_2O_3	2.55	1.30	0.55	-	12.30
Fe_2O_3	3.25	1.30	0.1	-	-
MgO	0.69	8.70	0.08	-	-
SO_3	0.66	2.80	52.56	55.16	-
Na_2O	-	-	0.03	-	-
K_2O	7.93	12.00	0.16	-	-
LOI	1.35	18.00		-	-

2.3.6 Effect of Curing Programme

- In Figure 2.6, the graph displays the compressive strength of metakaolin-based geopolymer binders, identified as G1 and G2. It demonstrates the variations in compressive strength over different curing periods, ranging from 7 to 56 days. The compressive strength values are as follows: G1 - 17.7 MPa, 19.0 MPa, 21.2 MPa, 29.9 MPa, and 32.8 MPa, while G2 exhibits strengths of 22.9 MPa, 27.63 MPa, 32.6 MPa, 36.0 MPa, and 39.7 MPa. These results illustrate a clear trend wherein the strength of geopolymer binders experiences a substantial increase as the curing period extends, progressing from 17.7 MPa to 32.8 MPa for G1 and from 22.9 MPa to 39.7 MPa for G2. This pattern implies that the polycondensation process occurring within the geopolymer structure is significantly improved as curing periods lengthen, signifying an increased dissolution of metakaolin particles. This observation aligns with the findings reported by Tchakoute et al. (2016).

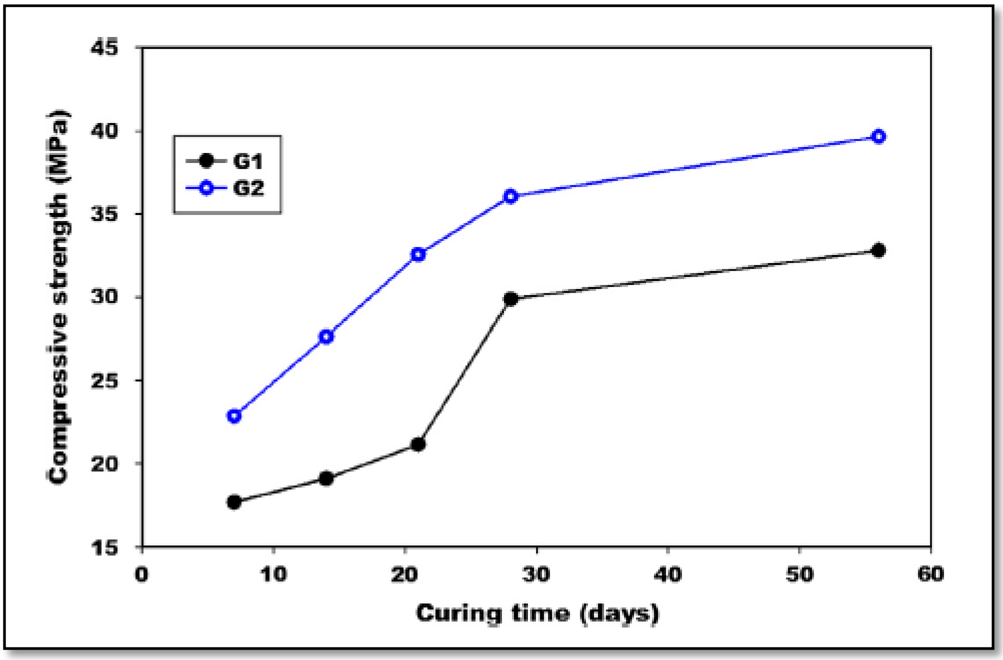

Fig: 2.6 Compressive strength of geopolymers G_1 and G_2 with various curing time (Tchakoute et al., 2016)

- Fig. 2.7 presents the effect of increased temperatures on the physical properties of geopolymer samples employing sodium (Na) and potassium (K) as activators. The graph reveals the occurrence of surface cracks in both types of geopolymers. Remarkably, no visible cracks are observed in either geopolymer up to a temperature of 400°C. However, a divergence in behavior is apparent as the temperature increases. For the sodium (Na)-based geopolymer, indications of surface cracking become apparent at 600°C, and this degradation significantly intensifies at 800°C, resulting in the formation of extensive and prominent cracks on the specimen’s surface. Conversely, the geopolymer incorporating potassium (K)-based activator demonstrates increased resilience against surface cracking, maintaining its integrity without any visible cracks up to 600°C. Yet, at 800°C, it does display the formation of fine cracks, though to a lesser extent compared to the Na-based counterpart. These observations align with the findings reported by Hosan et al. (2016).

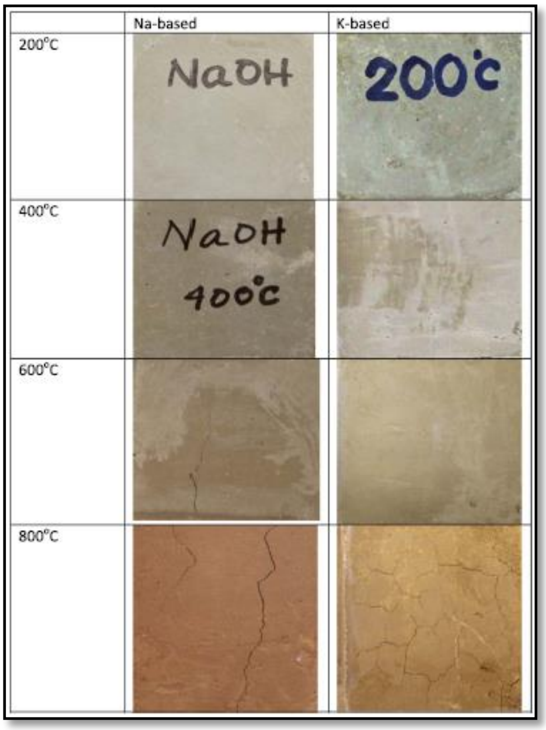

Fig: 2.7 Cracking behavior of fly ash geopolymer containing sodium – potassium-based activators at elevated temperatures (Hosan et al., 2016)

Table: 2.6 The Effect of Varying Curing Techniques on the Characteristics of Geopolymers

Geopolymer Type	**Curing Regimen**	**Compressive Strength (at Specified Age)**	**Principal Observations**
Geopolymer Utilizing Terracotta Roof Tile Waste (Usha et al., 2016)	Temperature range of 35°C to 75°C	26 N/mm² (at 28 days)	Optimal curing demonstrated at 65°C.
Fly Ash-Based Geopolymer (Giasuddin et al., 2013)	Initial 10-12-hour ambient temperature curing upon casting, followed by sequential curing in saline water, normal water, and sealed conditions	Compressive strengths ranging from 49-91 MPa	Superior performance noted in sequentially cured samples, particularly in selected condition curing.
Fly Ash-Based Geopolymer (Narayanan & Shanmugasundaram, 2017)	Varied curing methodologies at 28 days, including hot air oven, ambient, heat chamber, and autoclave curing	Compressive strengths at 29.27 MPa, 22.32 MPa, 23.91 MPa, 21.64 MPa	Hot air oven curing indicated as the most effective regimen.
Fly Ash-Based Geopolymer (Helmy, 2016)	Intermittent Curing Protocol at 70°C with a series of 4 intermittent heat curing steps each lasting 6 hours followed by 18 hours at ambient temperature	Compressive strength of 27 MPa	Intermittent curing regimen demonstrated optimal results.
Geopolymer developed from the Fly Ash (Adam and Horianto, 2014)	Temperature curing was conducted in the thermal range of 80°C to 120°C for durations of 4, 6, and 20 hours at the curing time of 3, 7, 14, and 28 days.	Compressive strength of 33 MPa at 7 days	Superior strength outcomes observed with 120°C heat curing for 20 hours.

Table: 2.6 Continued from the previous page

Geopolymer Type	**Curing Regimen**	**Compressive Strength (at Specified Age)**	**Principal Observations**
Fly Ash-Based Geopolymer (Nazari et al., 2011)	Curing methodology comprising an initial 24-hour curing period after casting, followed by 36 hours of oven curing at heat levels spanning from 50°C to 90°C	Compressive strengths within the range of 49-60 MPa	Curing at 80°C indicated as the optimal regimen.
Fly Ash-Based Geopolymer (Bakria et al., 2011)	Oven curing at varying temperatures, including 50°C, 60°C, 70°C, and 80°C for 24 hours at the 7th day	Compressive strength of 67.04 MPa	60°C temperature regime demonstrated optimal performance, with compressive strength diminishing at higher temperatures.
GGBFS-Based Geopolymer (Rajarajeswari and Dhinakaran, 2016)	Hot air oven curing within the temperature range of 60°C to 100°C	Compressive strength of 44.71 MPa	Optimal performance noted at 80°C, with reduced strength observed beyond this temperature.
POFA-Based Geopolymer (Salih et al., 2015)	Oven curing under ambient conditions, with degree of heat ranging from 60°C, 70°C, to 80°C	Compressive strength of 39.16 MPa at 180 days	Optimal performance observed at 70°C, with compressive strength declining beyond this temperature.
Metakaolin-Based Geopolymer (Yuan et al., 2016)	Curing temperatures within the range of 50°C to 80°C	Compressive strength of 62.6 MPa at 50°C and 106.2 MPa at 80°C	Maximum strength achieved at 80°C.

- The microstructure of the geopolymer experiences a progressive increase in density as the degree of temperature increases from 500°C to 800°C. This transformation is further substantiated by alterations in the apparent density within this specific temperature range. Notably, unreacted particles are discernible on the fracture surface, particularly in samples subjected to lower curing temperatures. These observations provide compelling evidence that the extent of the geopolymerization reaction is enhanced at elevated temperatures, in alignment with the concurrent changes in mechanical properties.
- Nevertheless, as mentioned previously, substantial porosity and cracks become evident in the samples cured at 90°C, likely attributed to water loss. When the geopolymer paste is subjected to a curing temperature of 90°C, while it may facilitate the extent of the geopolymerization reaction, it also accelerates the rate of water evaporation from the fresh paste compared to lower curing temperatures. This swift water evaporation results in the creation of a considerable quantity of voids and fissures within the resulting geopolymer framework, as recorded. This rapid water evaporation leads to the formation of a significant number of pores and cracks within the resulting geopolymer structure, as documented by Yuan et al. (2016)**.** Table 2.6 showing the effect of curing period on the properties of the geopolymer.

2.4 Utilization of Industrial waste through Geopolymerization

- In their recent study, Panigrahi et al. (2023) have investigated the use of pond ash as an innovative construction material with particular relevance to civil engineering. The research involved the strategic incorporation of red mud and slag into the pond ash, aimed at bolstering its structural strength and performance characteristics. This investigation holds promise for advancing the field of civil engineering materials.

- Kshirsagar and Hedge (2020) conducted a study in which they utilized pond ash as fine materials in concrete. Their research resulted in an impressive range of compressive strength, with values ranging from 43 to 45 MPa.
- Kalgal and Pranesh (2013) conducted an extensive durability investigation, examining the impact of various factors such as sulfate exposure, chloride exposure, acid attack, corrosion resistance, and permeability on concrete compositions that incorporated pond ash as a partial or complete replacement for sand. Their findings indicated that the performance of concrete incorporating pond ash was comparable to that of traditional concrete in regard to both strength and durability. It was observed that the loss of strength in concrete subjected to hydrochloric acid (HCl) immersion was generally more pronounced compared to concretes exposed to other solutions.
- Abhilash et al. (2016) Carried out an extensive analysis of the mechanical characteristics of geopolymer concrete when subjected to the substitution of cement with the mixtures of fly ash and ground granulated blast furnace slag (GGBFS) at various replacement levels (50:50, 75:25 & 100:0). In this study, sodium silicate ($Na2SiO3$) and sodium hydroxide ($NaOH$) were employed as alkaline activators, and the research extended over a period of 112 days. The primary finding of the study emphasized a significant decrease in compressive strength, split tensile strength, and flexural strength as the proportion of fly ash in the mixture increased from 50% to 100% as depicted in Fig. 2.8.

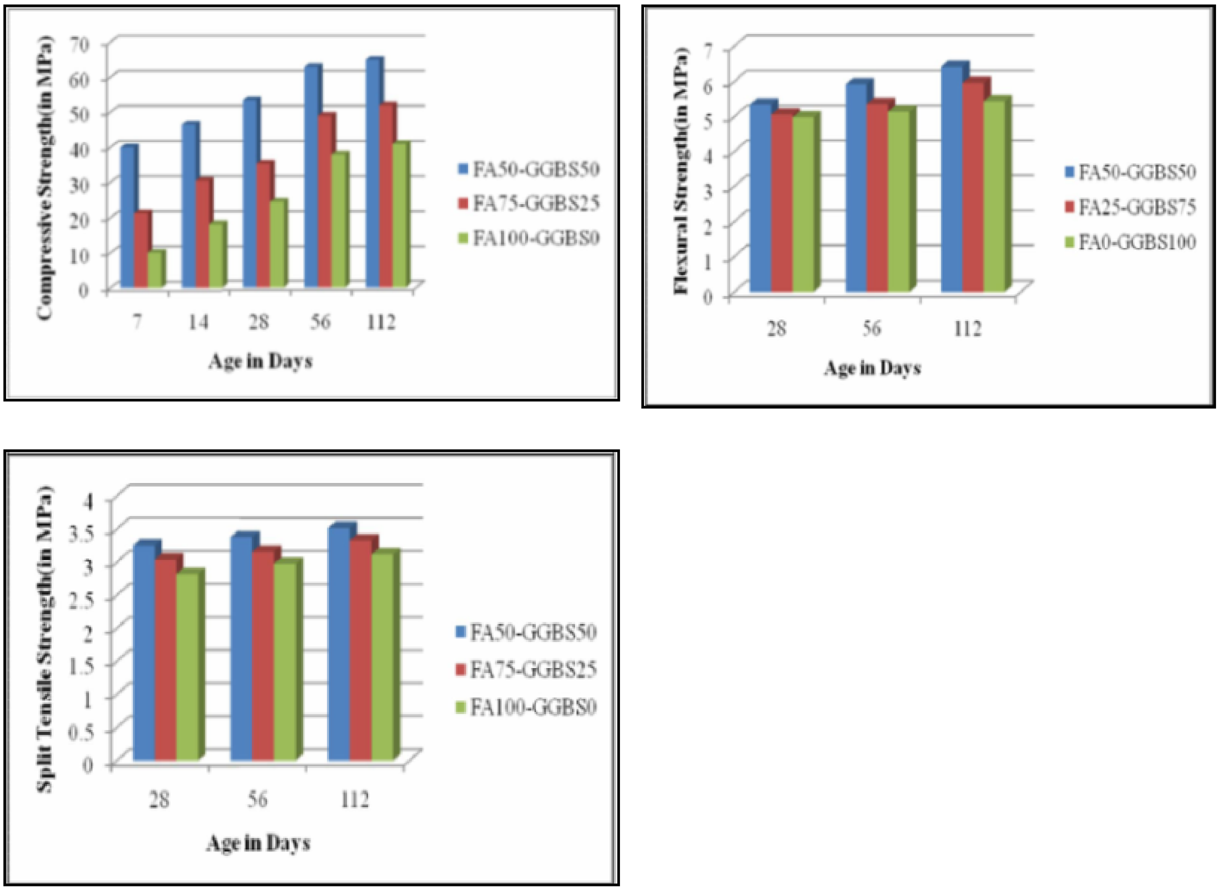

Fig: 2.8 Showing the reduction in compressive strength split tensile strength and flexural strength with increased percentage of fly ash from 50% to 100% (Abhilash et al., 2016)

- In a study by Rahim et al. (2014), an analysis of the mechanical and physical characteristics of fly ash-based geopolymer was performed. The research concentrated on modifying the solid to liquid ratio while using only sodium hydroxide as the activator. Notably, the study identified an optimal solid to liquid ratio of 4 for the chemical activator, which resulted in the highest achievable strength.
- Duan et al. (2016) conducted a study that involved investigating the mechanical and mineralogical properties of fly ash-based geopolymers mixed with silica fume, while subjecting them to cycle of heat curing. Their study entailed the creation of geopolymer specimens using alkali activation mixtures that combined fly ash with silica fume. Within

this investigation, fly ash was systematically substituted with silica fume, ranging from 10% to a maximum of 30%.

- Ranjbhar et al. (2014) explored the impacts and suitability of utilizing palm oil fuel ash (POFA) as a substitute material in fly ash-based geopolymer mortar. Their experiment revealed that the geopolymer developed from fly ash exhibited higher early compressive strength when compared to the geopolymer incorporating palm oil fuel ash.
- Mehta and Siddique (2017) conducted a study, in which low-calcium fly ash from thermal power plants was partially substituted (0%, 10%, 20%, and 30%) with Portland cement (OPC), and Natural sand from river was employed as both fine size and coarse size aggregates. Several tests were carried out to assess workability, compressive strength, split tensile strength, and rapid chloride permeability. The test results indicated that the rheological properties of low-calcium fly ash-based geopolymer exhibited a decrement with an escalation in OPC content. Conversely, the compressive strength of the geopolymer displayed an increment with the further incorporation of OPC, resulting in reduced permeability of the geopolymer.
- The compressive strength of unadulterated red mud and red mud subjected to flue gas desulfurization, combined with fly ash in a 50:50 proportion, exhibited strength of 15.2 MPa when treated with a 2.5 M NaOH solution, and 20.3 MPa when exposed to a 3.5 M NaOH solution, as determined by Nie et al. (2016).
- Red mud finds applications in various areas, including the manufacturing of construction materials such as bricks, cement production, glass ceramics production, water treatment, and utilization as a catalyst (Samal et al., 2013).
- Kalkan (2006) harnessed red mud as a stabilizer for crafting clay liners. The resulting mixture of red mud and cement demonstrated elevated compressive strength while

concurrently reducing hydraulic conductivity and swelling compared to natural clay samples.

- Yang et al. (2019) introduced a novel geopolymer formulation by combining red mud (in slurry form) with class F fly ash. This research delved into assessing the mechanical properties, volume variations, weight loss, and microstructural alterations of the resulting red mud-fly ash geopolymer. Remarkably, the RMFA geopolymer exhibited an impressive compressive strength exceeding 17 MPa.
- Zhang et al. (2014) pioneered the creation of a polymer utilizing both the Red Mud and Fly Ash. Their study delved into the impact of various synthesis factors on the mechanical properties (compressive strength), microstructure (mineralogical), and chemical composition of this innovative geopolymer. Significantly, the unconfined compressive strength at a 28-day curing period and an ambient temperature of 230°C displayed a variation within the range of 11.3 to 21.3 MPa.
- Another study, the utilization of red mud, combined with coal gangue and fly ash, was explored to develop a geopolymer. This investigation involved both the combination of coal gangue and red mud and the blend of coal gangue, fly ash, and red mud. The compressive strength of the binary combination of red mud and coal gangue was measured at 7.3 MPa, while the compressive strength of the ternary mix of coal gangue, red mud, and fly ash was determined to be 5.7 MPa (Koshy et al., 2019).
- Zhang et al. (2016) conducted research on the robustness and heavy metal leaching behavior of a red mud-class F fly ash geopolymer. The study revealed that the unconfined compressive strength, Young’s modulus, and flexural strength decreased by 30%, 70%, and 45%, respectively, after being soaked in sulfuric acid with a pH of 3.0 for 120 days.
- The geopolymer creation process incorporated the addition of silica fume to the red mud to enhance the silica/alumina ratio. When 25% of the red mud was substituted with silica

fume, the geopolymer achieved a 28-day compressive strength of 31.5 MPa (Ye et al., 2016).

- Rafeet et al. (2019) documented the mechanical properties of fly ash-GGBFS mixes and investigated the developed products.
- Saha and Rajasekaran (2017) observed improvements in the setting time and compressive strength of fly ash-based geopolymers through the integration of GGBFS. Meanwhile, Dev et al. (2014) reported advancements in the workability and compressive strength of class F fly ash concrete by incorporating GGBFS.
- Alam et al. (2019) investigated the enhancement of geotechnical properties of Red Mud a bauxite residue through the solidification of alkali-activated blast furnace slag.
- Zawrah et al. (2016) explored the potential of utilizing waste generated during brick production and including ground granulated blast furnace slag (GGBFS) at different ratios.
- Cheah et al. (2017) carried out an evaluation of the performance of an enhanced mixture, comprising ground granulated blast furnace slag (GGBFS) and high-calcium wood ash in 80:20 ratio. This blend was used in conjunction with ground fly ash, and a reduced amount of alkaline activator was employed in the activation process.
- Islam et al. (2014) conducted a study examining the impact of different proportions of three waste materials, namely Fly ash a coal combustion residue, palm oil fuel ash (POFA), and GGBFS, on the compressive (mechanical) strength of geopolymer mortar. They employed M-sand as the fine aggregate in their experiments.
- Junaid et al. (2021) Carried out a study to investigate the characteristics of ambient-cured alkali-activated blends (ABB) consisting of low-calcium fly ash (class F) and GGBFS.
- Geopolymers have attracted significant interest because of their impressive compressive strength, minimal permeability, exceptional reactivity, and remarkable fire resistance.

2.5 The Extent of usage of these industrial by-products in problematic soil

Priyadharshini et al. (2017) studied the importance of geopolymer technology in unutilized excavated soil (waste soil) obtained from construction activities like excavations, tunnelling, mining, dredging. With the developing infrastructure needs, the problem of illegal dumped excavated soil has become one of the important issues to be taken care with priority. Table 2.7 discussed the effect of various industrial waste i.e. GGBFS, ladle furnace slag, crumb rubber and fly ash on clay (Keramatikerman et al., 2016; Manso et al., 2013; Yadav and Tiwari, 2017 ; Ozdemir, 2016). The direct utilization of soft clay deposits, which are prevalent in floodplains, deltas, and coastal regions as noted in (Arulrajah and Bo, 2008, and Bo et al., 2015), in geotechnical engineering faces limitations because of their elevated moisture content and reduced bearing capacity (as indicated in Du et al., 1999; Omar et al., 2011; Liu et al., 2011, 2012; and Yu et al., 2016). In order to determine the feasibility of calcium carbide residue (CCR), Du et al. (2016) examined the in-situ development of soft highway subgrade soil that had been stabilized with CCR and revealed that by Kampala and Horpibulsuk (2013) soil stabilized with CCR exhibited relatively greater strength when compared to the soil stabilized with hydrated lime. In a study by Vakili et al. (2016), it was observed that the strength of cured cemented clay soil improved when a certain percentage of slag (GGBFS) and sodium silicate were added. The cohesion value increased from 44 kPa to 60 kPa when 5% of slag was added after 28 days of curing. The stability of embankments, including those supporting highways, railways, and various engineering structures built on soft soil, is vulnerable to the presence of weak, water-unstable clay aggregates. This susceptibility can lead to erosion during the wet season and potentially result in excessive settlement if suitable remediation measures are not implemented (Mirzababaei et al., 2017) and they also stressed on the influence of two polymers i.e. polyvinyl alcohol (PVA) and

1,2,3,4 Butane Tetra Carboxylic Acid (BTCA) on the engineering properties of the expansive soil.

Table: 2.7 Effect of industrial by product on the properties of soft soil (Keramatikerman et al., 2016; Manso et al., 2013; Yadav and Tiwari, 2017; Ozdemir, 2016)

Sr. no.	Soil type	Waste applied	Volumetric shrinkage	Compressive strength
01	Clay Keramatikerman et al. (2016)	GGBFS (ground granulated blast furnace slag)	Decreased from 23% to 18%	Increased from 0.5 MPa to 1.5 MPa
02	High plasticity type-CH Clay Manso et al. (2013)	Ladle furnace slag	Swelling reduced from 3.2% to 1.18%	Increased from 452 KPa to 1096KPa at 28 days
03	Soft soil Yadav and Tiwari (2017)	Crumb rubber + cement	Decreased	350KPa at 28 days
04	Soft soil Ozdemir (2016)	Fly ash	No significant change in the plasticity	642 KPa (at 10% fly ash) at 28 days

2.6 Research Gap

- The research carried out till now in the field of geopolymer uses various wastes, various alkali activators and various water-to-solid ratios in synthesizing the geopolymers. Several authors have incorporated additives at varying percentages, typically at 25%, 50%, 75%, and 100%. The primary choice for alkaline solutions among researchers has been a mixture of sodium silicate and sodium hydroxide at a different SS/SH ratio.
- It’s worth noting that no author has employed geotechnical methods such as MDD and OMC of mixes for geopolymer development. Additionally, using sodium hydroxide as the sole alkaline activator at different concentrations, ranging from low to high, has not been explored in past studies.
- Further, it is noticed that the use of the “reject fraction” of municipal solid waste (MSW) processing plants is challenging to minimise the environmental issues. Surprisingly, there

is currently a dearth of significant research focusing on MSW reject. This void in existing studies has provided the impetus to embark on the current research endeavour.

- Future researchers are encouraged to concentrate on the development of geopolymer concrete that approach depends on using a minimal amount of alkaline activator and subjecting the process to high-temperature treatment. This approach is crucial for the development of an environmentally sustainable product with a minimal embodied energy footprint, thereby contributing to environmentally responsible construction practices. Efforts should be directed toward the exploration of novel activation and curing methods, which may involve leveraging waste materials, such as sodic waste, or other substances possessing properties akin to commercial alkaline activators. Such innovative approaches have the potential to advance the field of geopolymer technology.

2.8 Summary

This chapter underscores the significant influence of several key factors on the compressive strength of geopolymers. These factors include the composition of the raw waste material, the type of alkaline solution employed, the concentration of the alkaline solution, and the duration of the curing periods. The specific hydration products responsible for the development of strength are contingent upon the composition of the waste materials. With these observations the research plan has been planned in detail in forth coming chapters.