

Investigating The Possibility Of Utilization Of Kaolin And The Potential Of Metakaolin To Produce Green Cement For Construction Purposes – A Review

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Abstract: Geopolymers are inorganic alkali aluminosilicate gels, formed from reaction of mineral clays or aluminosilicate-bearing industrial wastes, and treated with alkali silicate solution at 40 – 80°C. Geopolymers have been studied for several decades due to their excellent mechanical properties. They are suitable for use in construction and refractory applications. This paper summarizes some important research findings over the last 30 years and attempts to explain the chemistry and reaction mechanisms of the geopolymerisation process. Moreover, the paper emphasizes the potential to produce green cement powder from kaolin and metakaolin as an alternative to ordinary Portland cement (OPC).

Key words: Geopolymer; Green Cement; Cement Powder; Kaolin; Metakaolin.

INTRODUCTION

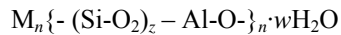
Ordinary Portland cement (OPC) is the highest volume engineering material in use today. However, growing concerns, in terms of both environmental impact caused by the extraction of raw materials and CO₂ emissions during cement manufacture, have spurred industries to reduce cement consumption by the utilization of supplementary materials. These materials may be naturally occurring, industrial wastes or by-products or those that require relatively less energy to manufacture (Sabir, 2001).

In order to address these concerns and other environmental problems relating to the disposal of waste industrial by-products while reducing costs, mixtures of Portland cement (PC) and pozzolans are commonly used. Metakaolin (MK), fly ash (FA), rice husk ash (RHA) and silica fume (SF) are used as partial pozzolanic replacements for cement in mortar and concrete and in the containment of hazardous wastes. Pozzolans have demonstrated advantages such as lower temperatures rise and improvements in durability and strength, although in some cases strength develops more slowly (Sabir, 2001). However, Tailby *et al.* (2010) reported that the preferential removal of systems from available Si due to geopolymer formation occurring more rapidly than cement minerals has retarded the development of C-S-H.

Another form of cementitious materials geopolymers was discovered by Glukhovskiy in the former Soviet Union in the 1950s (Sun, 2004). Davidovits (2002) conducted similar research in the late 1970s and initially reported on geopolymers in 1978. Geopolymer cements have been proposed as a more ecologically friendly alternative (Duxson, 2007) as their production does not involve limestone calcinations. Alkali-activated aluminosilicate binders are cement-like materials that can be formed by the reaction of calcined clays (e.g. metakaolin (Zhang, 2010; Murat, 1983; Cioffi, 2003; Wang, 2005; Duxson, 2007; Kong, 2007)) or industrial wastes (e.g. fly ash (Diaz, 2010; Kong, 2010; Guo, 2010; Temuujin, 2009; Temuujin, 2010) or metallurgical slag (Yunsheng, 2007; Chang, 2003)) with alkaline solution. Geopolymers or alkali activated cements contain aluminium and silicon species that are soluble in highly alkaline solutions. The dissolved species then undergo polycondensation to produce materials with desired mechanical properties (Sofi, 2007). They cure and set under ambient conditions into a material with an X-ray amorphous three-dimensional network of aluminate and silicate units with charge-balancing cation. While pozzolanic cements generally depend on the presence of calcium, inorganic polymers do not use the formation of calcium-silica-hydrates (CSH) for matrix formation and strength (Sofi, 2007).

Davidovits (Alonso, 2001; Alonso, 2001) described the alkaline activation in alkaline media (sodium and potassium hydroxide) in terms of a polymeric reaction characterized by the formation of materials with high mechanical strength. The inorganic polymers developed have the general formula:

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Where – is a bond; M is the alkali metal; z may be 1, 2, or 3 and n is the polymerization degree (Davidovits, 1991; Davidovits, 2008).

Compared to PC, manufacturing geopolymer cement requires a lesser amount of calcium-based raw materials, lower manufacturing temperature and lower amounts of fuel. This results in carbon dioxide emissions reduction as high as 80% - 90% (Bondar, 2005). Aluminosilicate geopolymers gain strength more rapidly than OPC and their ultimate strength can be higher and more cost-effective than OPC (Duxson, 2007). In most cases, 70% of final compressive strength is developed in the first 4 hours of setting. In comparison with PC, the geopolymer structure has lower permeability, resistance to fire and acid attacks, attains higher unconfined compressive strength, shrinks much less, has good resistance to freeze-thaw cycles and has excellent solidification of heavy metal ions (Davidovits, 1994).

Geopolymers are an effective application for high-strength concretes (strong resistance to chloride penetration, fire and/ or acid resistant coatings). They can be a good waste immobilization solution for the chemical and nuclear industries. They can be used for fire-resistant wood panels and decorative stone artifacts, fire-resistant composite for infrastructure repairs and upgrades, thermal shock refractory and etc (Davidovits, 2002). They can be utilized in many fields of industry such as civil engineering, automotive and aerospace, non-ferrous foundries and metallurgy, plastics, waste management, architecture and decoration and building retrofits (Zongjin, 2004).

2. Kaolin:

Kaolin is a soft, lightweight and often chalk-like sedimentary rock. It has an earthy odor with plate-like crystal morphology. The main constituent, kaolinite, is a hydrous aluminium silicate of approximate composition $2H_2O \cdot Al_2O_3 \cdot 2SiO_2$ (Prasad, 1991). Moreover, kaolin usually contains quartz and mica and less frequently feldspar, illite, montmorillonite, ilmenite, anastase, haematite, bauxite, zircon, rutile, kyanite, silliminate, graphite, attapulgite and halloysite (Varga, 2007). Kaolinite is aluminosilicate that structurally consists of alumina octahedral sheets and silica tetrahedral sheets stacked alternately. The shape of a perfectly ordered kaolinite crystal is pseudo-hexagonal, but ordering may range from a high degree, to a poorly ordered crystal where shape is non-determinant. Kaolin is one of the most versatile industrial materials (Prasad, 1991).

Davidovits (2008) primarily used kaolinite as source of alumino-silicate oxides to synthesize geopolymers. Kaolinite provides a structure-forming species to the overall geopolymerisation process. Van Jaarsveld *et al.* (2002) studied the effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers and found that different sources significantly affect the final properties of a geopolymeric material due to large part to the non-reactive nature of kaolinite in geopolymer samples. Unreactive clay particles could cause problems because of water absorption and retention. According to Xu and Van Deventer (2000), addition of kaolinite is necessary. But, the dissolution rate of Al from raw materials is insufficient to produce a gel of desired composition. Low-reactivity kaolinite requires enough time to interact among the source materials in order to reach the gel phase.

Xu and Van Deventer (2002) conducted research on the relative reactivity of different minerals presented in different ratios in kaolinite and stilbite mixtures. They found that the addition of kaolinite is necessary for the formation of gels for most of the aluminosilicate minerals. The authors also stated that if kaolinite is used in the absence of other aluminosilicates, a weak structure is formed. Thus, the interaction between different aluminosilicates seems to be quite important (Komnitsas, 2007).

3. Metakaolin:

Metakaolin is essentially an anhydrous aluminosilicate that is produced by the thermal decomposition of kaolin [20], a naturally occurring clay containing kaolinite, $Al_2Si_2O_5(OH)_4$ and trace amounts of silica and other minerals. The hydroxyl ions are strongly bonded to the aluminosilicate framework structure, thus only temperatures in excess of $550^\circ C$ can eliminate them. When large-layer structured materials such as kaolinite are subjected to intensive thermal treatment ($850^\circ C$), the material undergoes a series of transformations that enhance its subsequent reactivity with given chemical agents. At approximately $600^\circ C$, kaolinite loses most of its crystallinity. This implies that the hexagonal layer structure in the kaolinite is partially destroyed at this temperature. The original mineral structure becomes disorganized, forming the material referred to as metakaolin. Metakaolin is a partially ordered structure that cannot rehydrate in the presence of water (or does so very slowly). The exothermal dehydroxylation reaction is represented by Eq. (1) (Palomo, 1999):



Murat and Dirouche (Murat, 1983) found that between 730 °C and 760 °C, kaolin calcinations generated a high-disordered metakaolin that was more reactive. Due to its disorder and X-ray amorphous nature, it possesses a huge reactive potential when in the presence of an alkali/alkaline earth-containing solution. If metakaolin is mixed with specific amounts of NaOH solution or NaOH + sodium silicate solution (concentrations ranging from approximately 7 to 12 M) and then cured at a temperature below 100°C, it is possible to produce a solid that has an aluminosilicate network structure resembling a zeolitic material. Consequently, the solid possesses some interesting mechanical properties (Palomo, 1999).

The alkali activation of metakaolin is a way of producing high-strength cementitious materials. The use of calcined clays as a pozzolonic additive for cement has been accepted practice since Roman civilization (Palomo, 1999). Metakaolin improves mechanical strength (Cioffi, 2003), reduces the infiltration of water and salts through the sample and prevents the alkali-aggregate reaction from occurring (Palomo, 1999). Hongling *et al.* (2005) synthesized a metakaolinite-based geopolymer at about 20°C and found that the flexural strength, compressive strength and apparent density of the geopolymer increases with an increased concentration of NaOH. The authors concluded that the geopolymer is mainly amorphous, and the colloid reaction in the system mainly occurs at the surface of the microflake of the metakaolinite particulates.

Also, Cioffi *et al.* (2003) studied a geopolymer synthesized from calcined kaolinite, obtained by calcinations at temperatures ranging from 500°C to 750°C from 2 to 6 hours and polycondensation at temperatures ranging from 25 to 85°C. They proved that it is possible to produce good-quality building materials with this process. Similarly, in recent years, some studies (Sun, 2004; Zhang, 2010; Duxson, 2007; Kong, 2007; Duxson, 2005; Rovnanik, 2010; Zuhua, 2009) have been carried out on the alkaline activation of metakaolin to produce geopolymer cement.

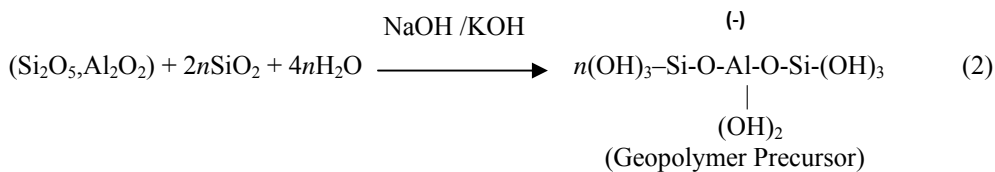
Moreover, Palomo *et al.* (1999) studied the chemical stability of cementitious materials based on metakaolin when exposed to aggressive solutions. They found that the aggressive solution had little negative effect on the evolution of microstructure and strength of the materials. Flexural strength slightly increased over a 90-day period and in older samples cured in sodium sulfate solutions. Some of the amorphous material present had crystallized to a zeolite-like material belonging to the faujasite family of zeolite. The amount of time the sample spends in the solution is responsible for a certain degree of transformation of the amorphous aluminosilicate network structure into a crystalline one.

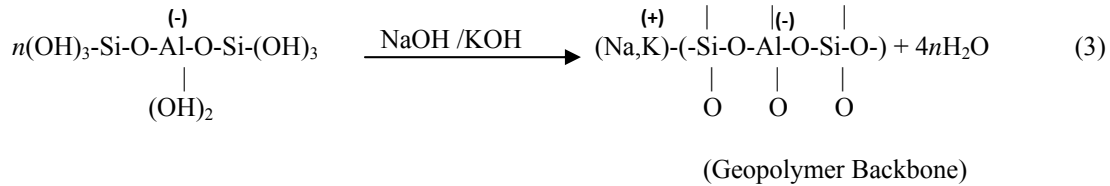
Other researchers have activated metakaolin in the presence of calcium hydroxide with a highly concentration alkaline solution. They observed that in addition to the main reaction product, sodium aluminosilicate, CSH gel is also formed as a secondary product (Alonso, 2001; Alonso, 2001). Other researchers have investigated the effect of adding carbonate minerals (calcite and dolomite) (Yip, 2008) and calcium silicate source (Yip, 2008) to geopolymerisation of metakaolin-based geopolymers.

4. Reaction Mechanism:

The mechanisms of the alkaline activation process are one of the more challenging fields to study. Essentially, it is a colloid reaction with low-water content in the system. According to Zuhua *et al.*, (2009) pure water cannot activate solid materials, except for those containing considerable OH⁻ anions. Aluminosilicates are mostly used in the reaction in solid powder, while the activator can be easily constituted by NaOH or KOH solutions, sodium silicate solution, or potassium silicate solution. Alkali hydroxide solution is required for the dissolution of raw materials; sodium or potassium acts as binder, alkali activator and dispersant or plasticizer (Komnitsas, 2007).

Based on Davidovits (1994, 1991) the geopolymer consists of a polymeric Si-O-Al framework, with the SiO₂ and AlO₄ tetrahedron linked alternately by sharing all the oxygen atoms; the negative charge on Al³⁺ in IV-fold coordination is balanced with the positive charge of alkali ions (Na⁺, K⁺) (Davidovits, 1994). Geopolymerisation is exothermic and the geopolymeric reaction can be expressed as in Eqn (2) and (3) (Davidovits, 1994; Davidovits, 1994).





Properties of the solid aluminosilicate will directly affect the dissolution process and the subsequent reaction. The liquid activator will partially or completely dissolve the solid raw material and determine the break and recombination of the aluminosilicate structure, polycondensation and charge balance in the reaction system (Wang, 2005).

Geopolymeric products do not have stoichiometric compositions; they are comprised of a mixture of amorphous to semi-crystalline and crystalline Al-Si particles (Davidovits, 1991). The structure of geopolymers depends on the condensation temperature. Amorphous polymers are obtained at temperatures ranging from 20 to 90 °C, while crystalline polymers are obtained at 150 to 200 °C (Davidovits, 1991; Cioffi, 2003).

The process evolution is suggested in three steps: 1) the dissolution of soluble species in the alkaline phase; 2) reorganization and diffusion of dissolved ions with the formation of small coagulated structures; and 3) the growth and condensation of these structures to form the hydrated products (Alonso, 2001; Alonso, 2001; Komnitsas, 2007; Dimas, 2009). According to Hongling *et al.* the steps probably occur simultaneously once the solid material mixes with the liquid activator. The exact separation of the steps is hard to discern and the partition here is only from the point of view of thermodynamics (Zuhua, 2009). This is also reported by Zongjin *et al.* (2004).

Xu and Van Deventer (2000) proposed the following reaction scheme for the polycondensation process in geopolymerisation:



In reactions (4) and (5), the amount of Si-Al material used depends on the particle size, the extent of dissolution of Al-Si materials and the concentration of alkaline solution. However, in reaction (6), geopolymers formation occurred; the time needed for Si-Al material to form a continuous gel depends on the raw material processing condition (Komnitsas, 2007). Other researchers have also studied geopolymer formation (Schmucker, 2005; Singh, 2005; Provis, 2005).

5. Properties of Geopolymer Cement:

The setting time of a geopolymer is measured using a Vicat needle (ASTM C191) (Wang, 2003). Two setting times are defined: (1) an initial set that occurs when the paste begins to stiffen considerably; and (2) the final set which occurs when the cement has hardened to the point at which it can sustain some load. According to Hardjito *et al.* (2008), the initial and final setting time of a geopolymer is important because it establishes the schedules for transport, placing and compaction of the geopolymer. The authors conducted research on the setting time of low-calcium fly-ash geopolymer mortar and found that the geopolymer paste could be handled for up to 120 minutes without any sign of setting, when the curing temperature ranged from 65°C to 80°C. The fly-ash geopolymer paste did not harden at room temperature for at least one day. Setting time is much faster if the curing temperature increases, due to an increased rate of chemical reaction that accelerates the hardening of geopolymer mortar. The same conclusion is reported by Wang and Cheng (2003), Nguyen *et al.* (2008) and Cheng (2003).

Setting time of geopolymer mortar depends on type of source materials, composition of alkaline liquid and ratio of alkaline liquid to source materials by mass and, critically, on curing temperature (Chanh, 2008; Cheng, 2003). Figure 1 shows that curing temperature significantly affects initial and final setting time of geopolymer mortar. Figure 2 shows the comparison between setting time of concrete made from geopolymer cements and PC (Davidovits, 1991). Geopolymer hardens more rapidly than OPC.

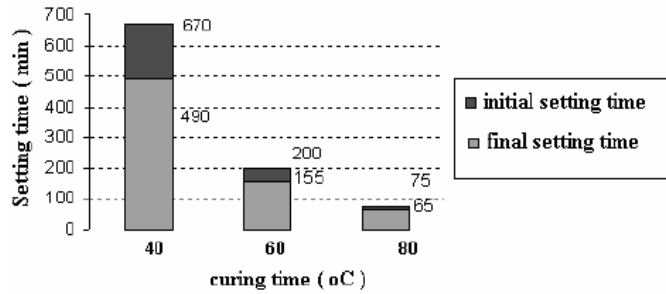


Fig. 1: Effect of curing temperature on setting time (Chanh, 2009).

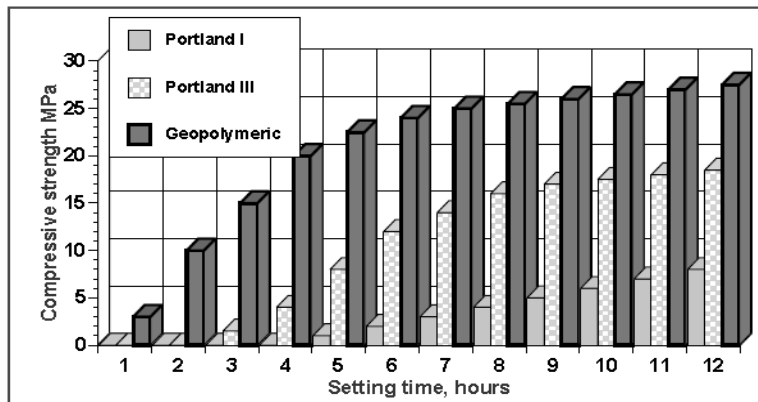


Fig. 2: Room temperature setting for concrete made of geo-polymer cements and Portland cements (Davidovits, 1991).

Based on Chindaprasirt *et al.* (2007), workability of a geopolymer depends on the concentration of NaOH and the sodium silicate to NaOH ratio. Increasing the sodium silicate to NaOH ratio decreased the flow of the geopolymer. However, a high sodium silicate to NaOH ratio (i.e. 3.00) requires extra water and superplasticizers to produce a flowable geopolymer. The authors also concluded that increasing the concentrations of NaOH solution and sodium silicate reduces the flow of the geopolymer. An increase in the NaOH concentration increases the viscosity of the solution and hence reduces the flow of the geopolymer. Sodium silicate is originally of very high viscosity solution, thus the increased amount of sodium silicate reduces the flow of the geopolymer. Similar results are obtained from the research conducted by Sathonsaowaphak *et al.* (2009). Figure 3 shows the flow with various (a) sodium silicate/10 M NaOH; (b) NaOH concentration; and (c) water/ash ratios.

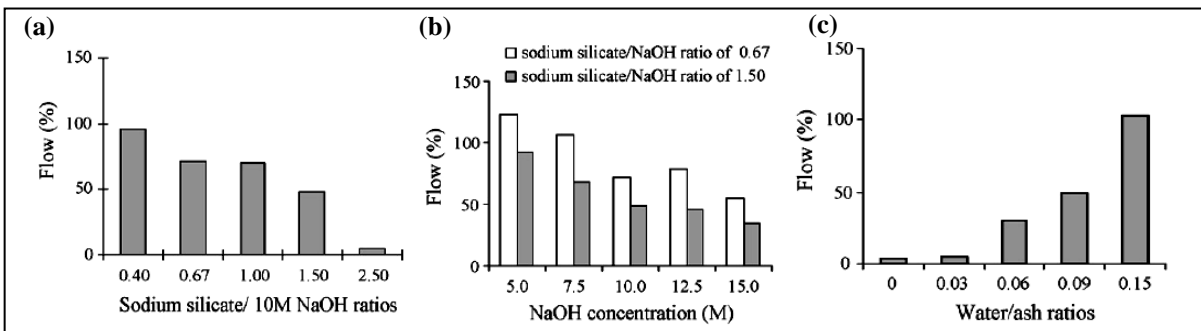


Fig. 3: Flow with various (a) sodium silicate/10 M NaOH; (b) NaOH concentration; and (c) water/ash ratios (Sathonsaowaphak, 2009).

6. Potential to Produce Green Cement Powder:

Figure 4 shows the production and processing of kaolin with different options. Kaolin is mixed with water and a small percentage of a chemical dispersant in a blunger. The kaolin lumps are broken into discrete individual particles (Murray, 2007). Then, the clay slurry is screened to remove grit. This is followed by de-watering of the slurry, which is achieved through thickening, filter pressing, extrusion of filter cake through screens and drying to approximately 10 % moisture content, producing kaolin noodles or powder (Reeves, 2006). The method for the synthesis of kaolin powder as described above can be applied to the synthesis of green cement powder. Raw materials (kaolin or metakaolin) are mixed with alkaline activator to produce geopolymer cement slurry. The geopolymer cement solid is then crushed and ground into fine cement powder after being dried in an oven at suitable temperature.

In order to successfully produce green cement powder from geopolymer, the cement powder must be able to mix well with water, and finally harden. As such, temperature plays an important role. In pottery clay making, parts of hand-built vessels are often joined together with the aid of slip, an aqueous suspension of clay body and water. The difference between fired and unfired clay is that unfired clay from the earth can be dampened with water. It is easy to manipulate and holds together as you shape it into an object.

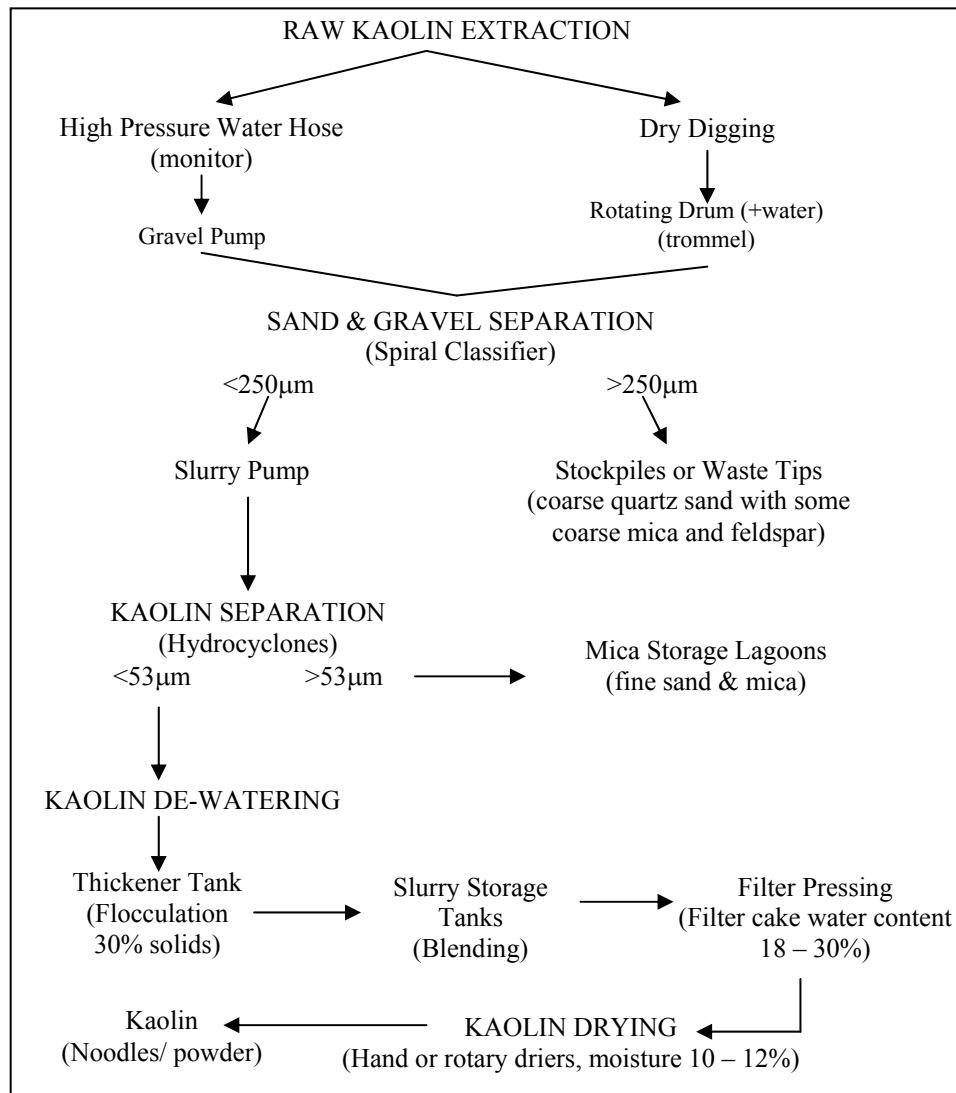


Fig. 4: Simplified kaolin production and processing flow diagram (Reeves, 2006).

After a few hours, the damp clay hardens into a leather-hard yet somewhat elastic stage, at which time decorative designs can be cut or etched into the clay surface. Once air-dried, green-ware clay is very fragile and crumbles easily. When subjected to the heat of a kiln (a high-firing oven), the clay piece becomes hard and permanent, and is capable of maintaining its form interminably. The firing process in the kiln converts the relatively weak green ceramic piece into a strong and durable product (Reeves, 2006). Once the ceramic body is fired, the process is irreversible. As kaolin and metakaolin are clay materials, they have the ability to mix with water and harden.

Also, for a thermoset resin, cure time is the time required for cross-linking reaction to take place. Curing transforms the resin into a plastic or rubber by a cross-linking process in the presence of energy and/or a catalyst. The extent of the cure reactions is usually described by the degree of cure (Campbell, 2004). The handling and processing of thermosets are very much dependent on gelation and vitrification. For example, thermosets are often identified at three stages of cure: A, B, and C. A-stage refers to an unreacted resin; B-stage refers to a partially reacted and usually vitrified system, below the gel point, which, upon heating to devitrify, may be processed and cured. Finally, C-stage refers to the completely cured network. Thus, B-staging often provides systems that are optimized for processing (Prime, 2009). Park and Kim (2000) analyzed development of domains during the curing process in partially cured thermoset resins using cloud point measurement and found that the unreacted thermoset monomer and partially reacted thermoset dimer or trimer exist simultaneously. Once completely cured, solid thermoset resins cannot be converted back to their original liquid form (Campbell, 2004).

We can transfer these established methods on clay pottery and thermoset resin to geopolymers. The geopolymer can be partially cured in an oven until a hard solid is obtained and crushed into fine cement powder. At this time, the geopolymer has only undergone partial geopolymerization and unreacted raw materials are presented. Once water is mixed with cement powder, the geopolymerization process continues and hardens in the presence or absence of heat (completely cured).

7. Conclusion:

This paper summarizes the research findings related to the synthesis of geopolymers. It attempts to explain the chemistry and reaction mechanisms and the potential to produce green cement powder. Most existing research has focused on applications of geopolymerisation; the mechanisms and reactions involved only recently have become the subject of detailed study. To date, there is no research on the manufacture of geopolymer cement powder. The hope is that this paper will help spur the development of green cement powder to replace OPC.

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