

DEVELOPMENT OF SUSTAINABLE CEMENTITIOUS MATERIALS

Zongjin Li,¹ Zhu Ding,¹ and Yunsheng Zhang²

¹Department of Civil Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

²Department of Material Science and Engineering, Southeast University, Nanjing, 210096, PRC

Abstract

In this paper, two types of sustainable cementitious composites, geopolymer and magnesium phosphate cement, are introduced. The geopolymer is a type of amorphous alumino-silicate products and magnesium cement is MgO based cementitious material. Geopolymer can be synthesized by polycondensation reaction of geopolymeric precursor, and alkali polysilicates. The MgO cement can be obtained by properly mixing MgO particles, fly ash, and phosphate. Comparing to portland cement, geopolymers and magnesium phosphate cement are energy efficient and environment friendly. Thus they are sustainable cementitious materials. In the paper, the recent developments of these two materials at HKUST are presented. The investigation shows that these two materials have superior properties to the portland cement such as high early strength, excellent volume stability, better durability, good fire resistance, and easy manufacture process.

1. Introduction

Portland cement (PC) concrete is the most popular and widely used building materials, due to its availability of the raw materials over the world, its ease for preparing and fabricating in all sorts of conceivable shapes. The applications of concrete in the realms of infrastructure, habitation, and transportation have greatly prompted the development of civilization, economic progress, stability and of the quality of life [1]. Nowadays, with the occurrence of high performance concrete (HPC), the durability and strength of concrete have been improved largely. However, due to the restriction of the manufacturing process and the raw materials, some inherent disadvantages of portland cement are still difficult to overcome. There are two major drawbacks with respect to sustainability. (1) About 1.5 tones of raw materials is needed in the production of every ton of PC, at the same time, about one ton of carbon dioxide (CO₂) is released into the environment during the production. Therefore, the production of PC is extremely resource and energy intensive process.

(2) Concrete made of PC deteriorates when exposed to the severe environments, either under the normal or severe conditions. Cracking and corrosion have significant influence on its service behavior, design life and safety.

Here, two different cementitious materials will be discussed. One is geopolymer and the other is magnesium phosphate cement (MPC). Compared with portland cement, the above two cements possess some common and individual characters, respectively. Their properties are very favorable to the sustainable development of our modern society.

1.1 Advantages and applications of geopolymer

Compared with portland cement, geopolymers possess the following characteristics:

- Abundant raw materials resources: any pozzolanic compound or source of silicates or almino-silicates that is readily dissolved in alkaline solution will suffice as a source of the production of geopolymer.
- Energy saving and environment protection: geopolymers don not require large energy consumption. Thermal processing of natural alumino-silicates at relative low temperature (600° to 800°) provides suitable geopolymeric raw materials, resulting in 3/5 less energy assumption than portland cement. In addition, a little CO₂ is emitted.
- Simple preparation technique: Geopolymer can be synthesized simply by mixing alumino-silicate reactive materials and strongly alkaline solutions, then curing at room temperature. In a short period, a reasonable strength will be gained. It is very similar to the preparation of portland cement concrete.
- Good volume stability: geopolymers have 4/5 lower shrinkage than portland cement.
- Reasonable strength gain in a short time: geopolymer can obtain 70% of the final compressive strength in the first 4 hours of setting.
- Ultra-excellent durability: geopolymer concrete or mortar can withdraw thousands of years weathering attack without too much function loss.
- High fire resistance and low thermal conductivity: geopolymer can withdraw 1000° to 1200° without losing functions. The heat conductivity of geopolymer varies form 0.24w/m·k to 0.3w/m·k, compared well with lightweight refractory bricks (0.3 w/m·k to 0.438 w/m·k).

Geopolymer, with properties such as abundant raw resource, little CO₂ emission, less energy consumption, low production cost, high early strength, fast setting. These properties make geopolymer find great applications in many fields of industry such as civil engineering, automotive and aerospace industries, non-ferrous foundries and metallurgy, plastics industries, waste management, art and decoration, and retrofit of buildings.

(1) Toxic waste treatment. Immobilization of toxic waste may be one of the major areas where geopolymer can impact significantly on the status quo. The molecular structure of geopolymer is similar to those of zeolites or feldspathoids, which are known for their excellent abilities to adsorb and solidify toxic chemical wastes such as heavy metal ions and nuclear residues. It is the structures that make geopolymer a strong candidate for immobilizing hazardous elemental wastes. Hazardous elements present in waste materials mixed with geopolymer compounds are tightly locked into the 3-D network of the geopolymer bulk matrix.

(2) Civil engineering. Geopolymer binders behave similarly to portland cement. It can set and harden at room temperature, and can gain reasonable strength in a short period. Some proportions of geopolymer binders have been tested and proved to be successful in the fields of construction, transportation and infrastructure applications. They yield synthetic mineral products with such properties as high mechanical performance, hard surface (4-7 on the Mohs Scale), thermal stability, excellent durability, and high acid resistance. Any current building component such as bricks, ceramic tiles and cement could be replaced by geopolymer

(3) Global warming and energy saving. It is well known that a great amount of CO₂ is emitted during the production of portland cement, which is one of the main reasons for the global warming. Studies have shown that one ton of carbon dioxide gas is released into the atmosphere for every ton of portland cement which is made anywhere in the world. In contrast, geopolymer cement is manufactured in a different way than that of portland cement. It does not require extreme high temperature treatment of limestone. Only low temperature processing of naturally occurring or directly man-made alumino-silicates (kaoline or fly ash) provides suitable geopolymeric raw materials. These lead to the significant reduce in the energy consumption and the CO₂ emission. It is reported by Davidovits [8] that about less 3/5 energy was required and 80%-90% less CO₂ is generated for the production of geopolymer than that of portland cement. Thus it is of great significance in environmental protection for the development and application of geopolymer cement.

(4) High temperature and fire resistance. Geopolymer cement possesses excellent high temperature resistance up to 1200° and endures 50kW/m² fire exposure without sudden properties degradation. In addition, no smoke is released after extended heat flux. The merits make geopolymer show great advantages in automotive and aerospace industries. At present, some geopolymer products have been used in aircraft to eliminate cabin fire in aircraft accidents.

(5) Archaeological analogues. It is proved that the micro-structure of hardened geopolymer materials is quite similar to that of ancient constructs such as Egyptian pyramid, Roman amphitheater. Consequently, many experts suspected that these

ancient constructs might be cast in place through geopolymerization, rather than made of natural stones. To confirm the viewpoint, many scientists make much attempt to explain the unsolved enigma for some ancient long-term constructs by means of geopolymer theories in recent years.

1.2 Advantages and applications of MPCs

MPCs are artificial stone made from acid-base reaction of magnesia and phosphates. They possess some properties that portland cements do not possess according to the previous studies. Therefore, they can be utilized in the field in which portland cements are not suitable [9-34]. (1) Very quick setting, high early strength. (2) Recycling lot of non-contaminated industrial waste to building material. (3) Recycling organic waste to building materials. (4) Stabilization of toxic and radioactive waste. (5) Very good durability, including chemical attack resistance, deicer scaling resistance, permeation resistance.

The applications of MPCs include following aspects:

(1) Due to its rapid setting and high early strength, magnesium phosphate cement (MPC) has been utilized in rapid repair of concrete structure, such as highway, airport runway, and bridge decks for many years. It can save a lot of waiting time and cost caused by long disrupting time by use other materials. If the interrupt period is too long for the busy highway, airport runway, and bridges, etc., it will cause lose of millions dollars. By using MPC materials, the interrupt time of transportation can be greatly shortened. Therefore, the valuable time and resource can be saved.

(2) MPC can incorporate with lot of non toxic industrial waste, such as Class F fly ash (FA) and translate it into useful construction materials. The addition FA in MPC can be over 40% by mass of MPC, about two times comparing with PC. In addition, MPC can combine the FA that is not suitable incorporated in PC because of its high carbon content and other impurities. Besides FA, even acid blast furnace slag, red mud (the residue of alumina industry), even tails of gold mine can also be utilized in MPC at large amount. These wastes are difficult to use in PC concrete in a considerable amount.

(3) Due to the high alkali environment of PC (pH over 12.5), when they are use as reinforcement, some components natural fibers, notably lignin, and hemicellulose will be susceptible to degradation. However, the lower alkalinity of MPC matrices (pH value 10 to 11) makes them potentially better suited to vegetable fiber reinforcement. Furthermore, the sugar in some natural fibers, such and sugarcane and corn stalk can prohibit the setting of PC, and weakens the bonding between portland cement and fiber. But, the set of MPC is not influenced by sugar.

(4) Management and stabilization of toxic and radioactive wastes, including solids and liquids. The wastes can be micro and /or macro-encapsulated and chemically bonded by MPC, form a strong, dense and durable matrix that stores the hazardous and radioactive contaminants as insoluble phosphates and microencapsulates insoluble radioactive components. The waste forms are not only stable in groundwater environments, but also are non-ignitable and hence safe for storage and transportation.

(5) Very suitable for repairing of the deteriorated concrete pavements in the cold areas. MPC can develop strength at low temperature due to its exothermic hydration and low water to binder ratio. At the same time, MPCs possess a higher deicer scaling property than portland cement.

(6) The raw material of MPC is hard burnt magnesia. In fact, it is a refractory material. Therefore, MPC can be designed to be fire proof and/or as cold setting refractory according to the practical need.

2. Summary on Geopolymer Development

2.1 Work done by others

Since France scientist Davidovits invented geopolymer materials in 1978 [35], great concerns on the development of geopolymer have been received across the world. More than 28 international scientific institutions and companies have presented updated research and published their results in public journals. These works mainly focus on the following aspects:

(1) Solidification of toxic waste and nuclear residues

Davidovits et al. [36] firstly began to investigate the possibilities of heavy metal immobilization by commercial geopolymeric products in the early 1990s. The leachate results for geopolymerization on various mine tailings showed that over 90% of heavy metal ions included in the tailings can be tightly solidified in 3D framework of geopolymer. In the middle of 1990s, J.G.S. Van Jaarsveld and J.G.S. Van Deventer et al. [37-40] also set out to study the solidification effectiveness of geopolymer manufactured from fly ash. The bond mechanism between heavy metal ions and geopolymer matrix is also simply explained on the basis of the XRD, IR, MAS-NMR and leaching results. Recently, the European research project GEOCISTEM [41] successfully tested geopolymerization technology in the context of the East-German mining and milling remediation project, carried out by WISMUT. Another research project into the solidification of radioactive residues was jointly carried out by Cordi-Geopolymer and Comrie Consulting Ltd., and was documented in reference [42].

(2) Fire resistance

Recently The Federal Aviation Administration (FAA), USA, and the Geopolymer Institute of Cordi-Geopolymere SA, France [43], have jointly initiated a research program to develop low-cost, environmentally-friendly, fire resistant matrix materials for use in aircraft composites and cabin interior applications. The flammability requirement for new materials is that they withstand a 50 kW/m^2 incident heat flux characteristic of a fully developed aviation fuel fire penetrating a cabin opening, without propagating the fire into the cabin compartment. The goal of the program is to eliminate cabin fire as cause of death in aircraft accidents. As with this program, the fire resistance properties of geopolymer reinforced by various types of fiber such as carbon fiber, glass fiber, SiC fiber etc. were tested and the fire-proof mechanics were also analyzed. In addition, the comparisons were made among geopolymer composite and carbon-reinforced polyester, vinyl, epoxy, bismaleinide, cyanate ester, polyimide, phenolic, and engineering thermoplastic laminates. The test results showed that these organic large molecular polymers ignited readily and released appreciable heat and smoke, while carbon-fiber reinforced Geopolymer composites did not ignite, burn, or release any smoke even after extended heat flux exposure. On the basis of these fireproof studies, some non-flammable geopolymer composites for aircraft cabin and cargo interiors were produced and introduced on November 18, 1998, in Atlantic City, NJ, USA.

(3) Archeological research

In the 1970s Professor J. Davidovits proposed a controversial theory that documented in a book [44] and has since gained widespread support and acceptance. He postulated that the great pyramids of Egypt were not built by natural stones, but that the blocks were cast in place and allowed to set, creating an artificial zeolitic rock with geopolymerization technology. He collected a great amount of evidences which come from old ancient Egyptian literatures and samples in sites to confirm his geopolymerization theory. From then on, many experts began to focus their concerns on geopolymer studies. Some related papers [45-55] and patents were also published.

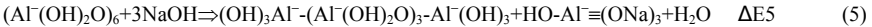
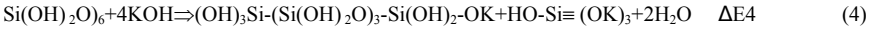
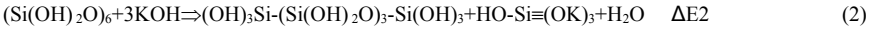
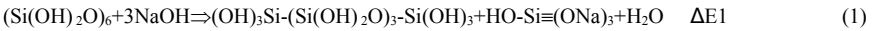
2.2 Work done by us

In 2002, Prof. Sun Wei from Southeast University and Prof. Zongjin Li from Hong Kong University of Science and Technology jointly applied for a research project to systematically investigate the synthetic mechanism, structural nature, proportional design method, mechanical and durability performance of geopolymer manufactured with naturally occurring and man-made alumino-silicate materials in China. Subsequently, the project (No.50278018) was approved by the China National Science Fund Committee. In fact, studies on geopolymer started in the early 2000. Many works on geopolymer have been done in three years. The following summarizes some of the experimental results.

(1) Reaction mechanism

Much attempt on formation mechanism has been made since the invention of geopolymer. However, only one described formation mechanism was proposed by Davidovtis. He believed that the synthesis of geopolymer consist of three steps. The first is dissolution of alumino-silicate under strong alkali solution. The second is reorientation of free ion clusters. The last is polycondensation. But each step includes many pathways. Taking dissolution step for example. It includes 8 pathways according to the thermodynamics. Different pathway can create different ion clusters that directly determine the final properties of geopolymer. Thus it is very important to understand the actual pathway for producing geopolymer in order to gain insight into the mechanism of geopolymerization. However, until now, these studies are not still done. It is because that the forming rate of geopolymer is very rapid, as a result, these three steps take place almost at the same time, which make the kinetics of these three steps inter-dependent. Thus it is impossible to separate these steps in experimental studies. This leads to the use of molecular simulation to solve these problems.

In our studies, two 6-membered-rings molecular structural models to represent the chemical structure of metakaolinite (main raw material for synthesizing geopolymer) were established in order to quantitatively analysis the formation process of geopolymer, as shown in Fig. 1(a), and Fig. 1(b). Based on these two 6-membered-rings models, all possible dissolution pathways of metakaoline under strongly alkali environment were numerically simulated using quantum mechanics, quantum chemistry, computation chemistry and thermodynamics theories. All possible pathways (Eqs. (1) to (8)) involved in the formation process of geopolymer were analyzed, and the enthalpies of each possible pathway were also calculated (Table 1). As a result, the optimum pathways in theory, that is the actually occurring pathways in the geopolymerization process, were determined. During molecular simulation, some interesting phenomena were found, and were explained by experimental results.



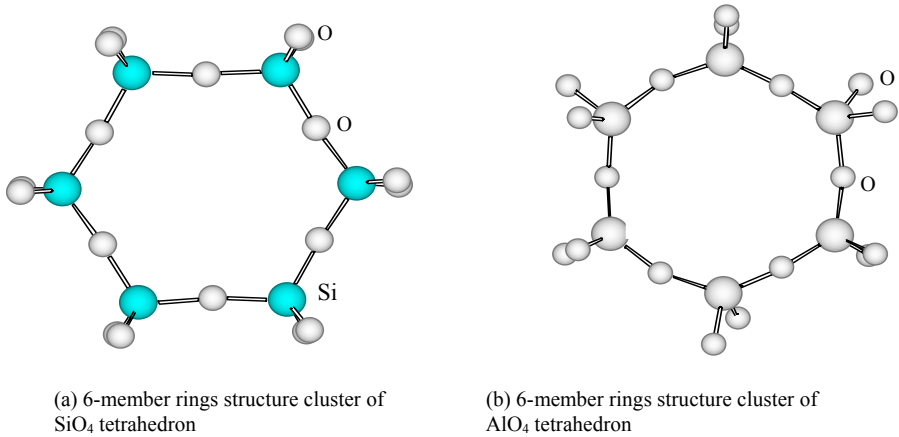


Fig. 1: Molecular structure representing model of metakaolinite

(2) Microstructure characterization

The structure characteristics of products directly determine the final mechanical and durability properties. The case is also true for geopolymer. Many researchers have investigated its microstructure using different advanced techniques. But because geopolymer is a type of amorphous 3D materials with complex composition, It is very difficult to quantitatively measure the exact arrangement and chemical atmosphere of different atomic in geopolymer. If we want to solve this difficulty, we should have to turn to statistical theories for establishing its molecular model. But unfortunately, until now, these studies are not still been done. Therefore, the structural nature of geopolymer is not yet understood thoroughly.

In our studies, many microstructure techniques, such as XRD, IR, XPS, MAS-NMR, ESEM-EDXA and TEM were used to investigate the structural characterization in atomic, molecular, nanometer, micrometer and centimeter scales. The relationship between geopolymers and the corresponding zeolites were also investigated. The inter-transformation between geopolymers and zeolites can be realized under specified conditions. On basis of these results, the micro-structure of geopolymers can be clearly characterized: geopolymer is an amorphous 3D alumino-silicate material, which is composed of AlO_4 and SiO_4 tetrahedra lined alternatively by sharing all oxygen atoms. Positive ions (Na^+ , K^+) are present in the framework cavities to balance the negative charge of Al^{3+} in four-fold coordination. In addition, 3D statistical models (Fig. 2) were also simulated according to the decomposition results of MAS-NMR spectra.

Table 1: Reaction heat of single 6-member rings structure model under strongly alkaline solution.

a. Single 6-member rings of SiO₄ tetrahedra

The molecular structural unit	Formation enthalpy (a.u)	Reaction enthalpy (kJ/mol)			
		$\Delta E1$	$\Delta E2$	$\Delta E3$	$\Delta E4$
(Si(OH) ₂ O) ₆	-1491.44763	-5.48908	12.12039	-36.22681	-19.22697
(OH) ₃ Si-(Si(OH) ₂ O) ₃ -Si(OH) ₃	-1294.64502				
(OH) ₃ Si-(Si(OH) ₂ O) ₃ -Si(OH) ₂ -ONa	-1385.43022				
(OH) ₃ Si-(Si(OH) ₂ O) ₃ -Si(OH) ₂ -OK	-1370.88091				
HO-Si≡(ONa) ₃	-500.93548				
HO-Si≡(OK) ₃	-437.84919				
NaOH	-119.29816				
KOH	-104.13922				
H ₂ O	-59.25069				

b. Single 6-member rings of AlO₄ tetrahedra

The molecular structural unit	Formation enthalpy (a.u)	Reaction enthalpy (kJ/mol)			
		$\Delta E5$	$\Delta E6$	$\Delta E7$	$\Delta E8$
(Al(OH) ₂ O) ₆	-619.66576	-299.7974	-245.78806	-302.69174	-235.0346
(OH) ₃ Al ⁻ -(Al ⁻ (OH) ₂ O) ₃ -Al ⁻ (OH) ₃	-776.45042				
(OH) ₃ Al ⁻ -(Al ⁻ (OH) ₂ O) ₃ -Al ⁻ (OH) ₂ -ONa	-839.39222				
(OH) ₃ Al ⁻ -(Al ⁻ (OH) ₂ O) ₃ -Al ⁻ (OH) ₂ -OK	-810.58557				
HO-Al ⁻ ≡(ONa) ₃	-441.65654				
HO-Al ⁻ ≡(OK) ₃	-342.17037				
NaOH	-119.29816				
KOH	-104.13922				
H ₂ O	-59.25069				

(3) Mechanical properties

More concerns have been received on the solidification of heavy metal ion and nuclear waste and fire resistance since 1990, but at present, less experimental data is available for the systematical investigation on mechanical properties and durability.

Up to now, more than 100 geopolymer concrete specimens were prepared to study mechanical behaviors such as compressive, flexural, splitting tensile, shear strength and their stress-strain responds. PSS geopolymer concrete has the highest mechanical performance among various geopolymer concretes, next to PSDS, and PS has the lowest strength.

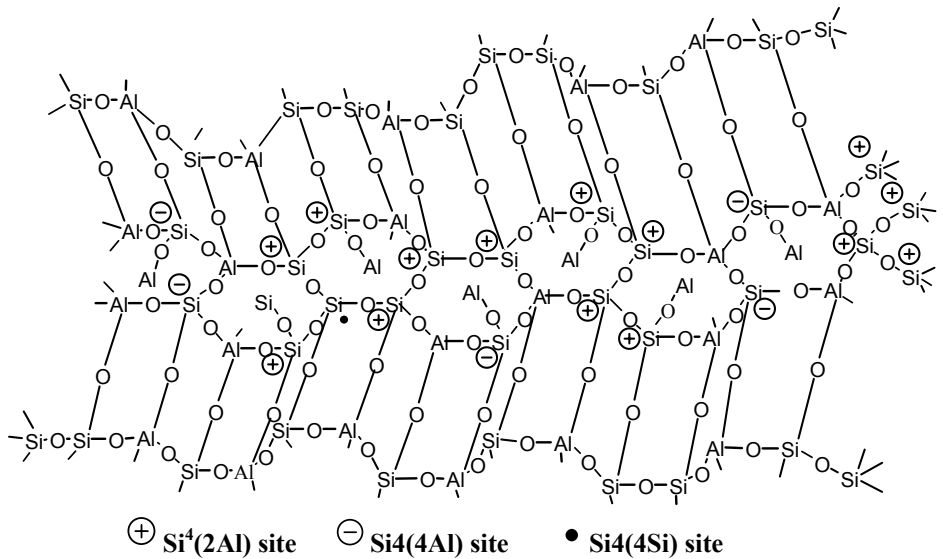


Fig. 2: Statistical structure model of K-Geopolymer

Another 147 geopolymer concrete or mortar specimens were also produced to investigate the durability properties such as chloride ions permeability, resistance to freezing and thawing cycles, resistance to chemical attack including HCl, H₂SO₄ and Na₂SO₄ attack, long-term volume stability, and alkali aggregate reaction (AAR). At present, the durability tests are still under way.

3 The Development of MPCs

3.1 Work done by others

The phosphate bonding has been known for about a century, since the advent of dental cement formulations. In refractory industry, the properties of cold-setting and heat-setting compositions were used as chemically bonded refractory. According to the comprehensive studies of Kingery in 1950, The phosphate bonding can be classified as (1) zinc-phosphate bond, (2) Silicate-phosphoric acid bond, (3) oxide-phosphoric acid bond, (4) acid phosphate bond, and (5) metaphosphate/polyphosphate bond [9]. The oxides such as magnesium, aluminum, zirconium, will react with phosphoric acid or acid phosphate at room temperature, forming a coherent mass, setting quickly and giving high early strength. The hydration system based on magnesia and ammonia phosphate [9-34] had drawn most of the attention in the past years.

From 1970s, many patents using the reaction of magnesia and acid ammonia phosphate have been granted for rapid repair of concrete. The variation in patents arises from the use of different raw materials, inert materials to reduce cost, and retarders to control the reaction rate. Most claims are supported by a few examples cited in the patents without systematic scientific approach. From the middle of 1980s, systematic studies about the system of magnesia and ammonia phosphate were made by researchers [9-32]. The hydration products, setting process, and strength development were the main content among those previous investigations. Very few papers focused on the durability of the system [17, 21, 32]. Entering the middle of 1990s, it was found that MPC can incorporate with lot of industrial waste and solidify toxic waste [33-35]. Therefore, MPC became a forceful candidate for sustainable development. The benefits in environment may be obtained from two aspects, (1) the non-toxic industrial waste can be recycled to useful building materials, and (2) many toxic and radioactive wastes treated difficultly with traditional process can be treated by MPC easily. This function endues MPC more promising use in the future, especially to the sustainable development of the modern society.

About the durability of MPCs, research work had been done by other investigators mainly includes, superior durability such as freezing-thawing and scaling resistance, protection steel from corrosion, better bond properties with waste organic materials, transfer non-contaminated industrial wastes into useful construction materials, and stabilization of toxic or radioactive wastes.

The deterioration of concrete pavements is mainly cause by frost action in cold areas. It is severely amplified by the use of deicer chemicals. The repair material must possess high frost/deicer-frost resistance. The result shown that MPC have very high deicer-frost resistance [17, 32]. The scaling does not occur on the surfaces of MPC materials until 40 freeze-thaw cycles. The regime of freeze-thaw cycling was achieved with cooling rate of about $0.5^{\circ}\text{C}/\text{min}$. for 4 hours at $-20\pm 2^{\circ}\text{C}$ and then thawed for 4 hours at $20\pm 5^{\circ}\text{C}$. A 3% NaCl solution was used as the deicer solution. The studies shown that the freezing thawing resistance of MPCs was basically equal to the well air-entrained PC concrete in general.

Steel corrosion in PC concrete was a very serious problem. However, MPC is inhibitor of corrosion of steel, forming an iron phosphate film at the surface of the steel. The pH of hardened MPC mortar is 10 to 11, this may be considered as contributing to inhibition of reinforcing steel corrosion. In addition, the ratio of permeability of MPC to PC concrete is 47.3%, or more than double in resistance to permeation [17]. Abrasion resistance test shown that MPC mortar possesses approximately double the abrasion resistance compared with slab-on-grade floor concrete and to be nearly equal to that of pavement concrete [17, 21]. With respect to

chemical corrosion resistance, in the case of continuous immersion of specimens in sulphate solution and potable water, results indicate that MPC mortar patches will practically remain durable under sulfate and moist conditions.

A wide range of waste particle sizes can be utilized when producing structural products using the MPC. Styrofoam materials are the candidate for optimal results. The styrofoam articles can be completely coated with a thin, impermeable layer of the MPC. The uniform coating of the styrofoam particles not only provides structural stability but also confer resistance to fire, chemical attack, humidity and other weathering conditions. The styrofoam insulation material provides superior R values. Furthermore, wood waste (suitable size range from 1 to 5 mm long, 1 mm thick and 2 to 3 mm wide) can be bonded with MPC to produce particleboard having flexural strength. For example, samples containing 50wt% of wood and 50wt% of binder display approximately 10.4 MPa in flexural strength. Samples containing 60wt% and 70wt% of wood exhibit flexural strength of 2.8 and 2.1 MPa, respectively. Once the wood and binder is thoroughly mixed, the samples are subjected to pressurized molding on the order of approximately 18.3 MPa, and for approximately 30 to 90 minutes.

With the progress of modern civilization, the living conditions had been greatly improved; at the same time, however, a large amount of industrial waste (including toxic and nontoxic) had been produced. MPC can bind lot of bind non-toxic industrial waste to useful construction materials. If the wastes were toxic, MPC can solidify and stabilize them. There is a significance to recycle and/or stabilize the waste, especially under the condition of natural resources becoming more and more deficient. The waste in various forms in aqueous liquids, inorganic sludge, particles, heterogeneous debris, soils, and organic liquids. However, there was only a few part of the total waste can be recycled, such as fly ash, red mud was manufactured blended portland cement or concrete. Most of the wastes need to be solidified and stabilized. Because of the divers nature of the physical and chemical composition of these wastes, no single solidification and solidification technology can be used successfully treat and dispose of these wastes. For example, the low-level wastes contain both hazardous chemical and low-level radioactive species [33]. To stabilize them requires that contaminants of two kinds be immobilized effectively. Generally, the contaminants are volatile compounds and hence cannot be treated effectively by high-temperature processes.

In a conventional vitrification or plasma hearth process, such contaminants may be captured in secondary waste stream or off-gas particulates that need further low-temperature treatment for stabilization. Also some of these waste streams may contain pyrophorics that will ignite spontaneously during thermal treatment and thus cause hot spots that may require expensive control system and equipment with demanding structure integrity on. Therefore, there is a critical need for a low-

temperature treatment and stabilization technology that will effectively treat the secondary wastes generated by high-temperature treatment process and waste that are not amenable to thermal treatment. Now, those wastes can be successfully solidified by magnesia phosphate cement, or chemically bonded phosphate ceramics (CBPC) [33]. Other forms of waste, such as ashes, liquids, sludge and salts can be also solidified by MPC.

MPC is very extremely insoluble in ground water and this will protect ground water from contamination by the contained wasted. The long-term leaching tests conducted on magnesium phosphate systems shown that these phosphate are insoluble in water and brine. The radiation stability of MPC is excellent [34]. Changes in the mechanical integrity of the materials were not detected after gamma irradiation to cumulative dosage of 10^8 rads.

3.2 Work done by HKUST

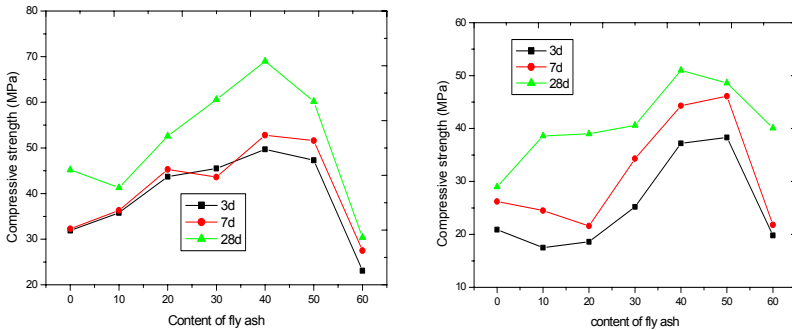
From the late of 2001, we started the project of new MPC system based on potassium phosphate. The main advantages of new system are binding lot of industrial waste and no ammonium gas was emitted. Up to now, the mechanical and chemical properties, hydration process and mechanism, durability and binding properties with old PC concrete had been investigated. Here the mechanical property and durability will be mainly introduced.

3.2.1 Mechanical properties

(1). Strength development of MPC made of different hard burnt magnesia

Two kinds of hard burnt magnesia and a Class F fly ash (FA). The magnesia contains 89.6% magnesium oxide was named M9, whose average size of particle was 30.6 μm . The other contains 71.6% magnesium oxide was named M7, whose average size of particle was 59.8 μm .

Compressive strength versus fly ash content for MPC mortars at 3, 7, and 28 days is presented in Fig. 3 for M7 and M9 series. From the figures, it can be seen that for the two series, the MPC mortars with 30%-50% fly ash exhibit higher strength than the sample without fly ash, and the highest strength occurred at the samples with 40% fly ash. To the mortars made from M9, from 10%-40% of FA, the strength gradually increases with the addition of fly ash at all ages (except M9F1 at 28 days has lower strength than that of M9F0). When the fly ash content surpasses 40%, the strength decreases. But, the strength of sample with 50% fly ash is still comparable to that of sample with 30% fly ash.

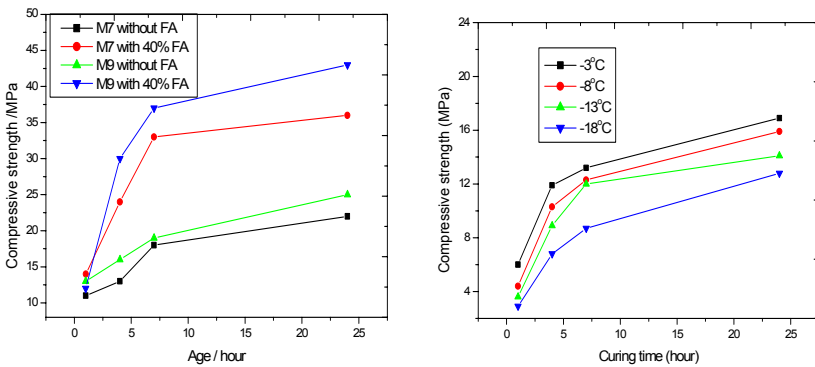


(a) M9 series sample (b) M7 series sample

Fig. 3: Strength development of MPC mortar sample

The modulus of elasticity of MPC mortar M9F0 and M9F4 was determined at age of 7 days. The elastic modulus of M9F0 and M9F4 is 27.47 and 31.85 GPa, respectively.

The compressive strength of MPC mortar at 1, 4, 7, and 24 hours under room temperature is shown in Fig. 4 (a). The specimens containing 40% FA had very fast development of strength than the specimens not containing FA, And Fig. 4 (b) was the strength development of MPC (AF content was 40%) mortar at 1, 3, 7, and 24 hours under negative temperature (After the specimens were formed they were put into the environmental chamber immediately together with molds. And they were demolded after one hour.) The test results show that FA has the effect of reinforcement to strength, even if MPC mortar were cured under very low temperatures.



(a) Cured in room temperature (b) Cured in negative temperatures
Fig. 4: Early strength development of MPC under different temperatures

3.2.2 Durability

(1) Deicer frost scaling resistance

The deicer used here is calcium chloride (CaCl_2) and the concentration in water is 4% by weight of water. The MPC mortar sample and PC mortar samples together immersed completely in CaCl_2 solution in a plastic box, which has no cover. Then the box was placed inside the environmental room, KATO for freezing and thawing. After these samples were frost (-18°C) for 16 hours, they were removed from the environmental room and placed in laboratory air at normal condition for 8 hours, which is a freezing-thawing cycle. Add water each cycle as necessary to maintain the proper depth of solution. Repeat the cycle daily. The surfaces of samples were flushed off thoroughly at the end each 5 cycles. Compressive strength was determined of MPSC mortar after following every curing stage: (I) The sample of MPSC mortar formed after 3 days, and 7 days for PC mortar; (II) These samples were suffered 30 freezing-thawing (FT) cycles; (III) The same above samples were cured 30 days under normal conditions; (IV) After that, the samples were tested after aging 60 days under normal condition.

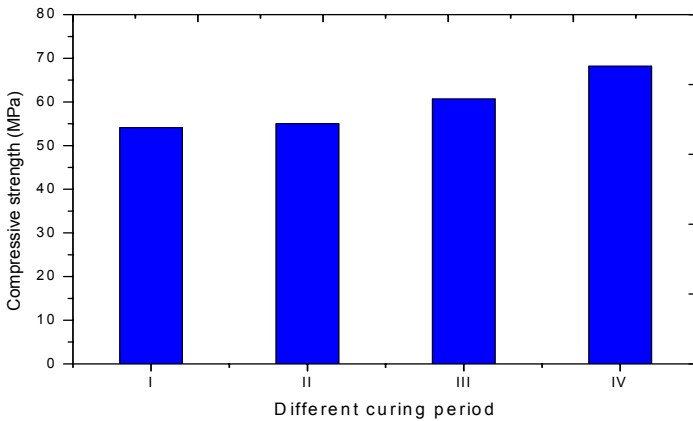


Fig. 5: Strength of MPC after FT salt scaling cycles

The compressive strength of MPC mortar was 54.1 MPa after hydration 3 days, and strength of PC mortar was 59.8 MPa for after hydration 7 days. They had the comparable strength when they were suffered FT cycles at same time. After 30 FT cycles, the surface of PC mortar samples were severe scaled and cannot be used to determine compressive strength (due to the very rough surfaces). However, the surface of MPC mortars is intact, smooth as the surfaces before FT cycles. This indicates that MPSC mortar has a superior deicer scaling resistance to PC mortar. The compressive strength test result, Fig. 5, showed that the strength of MPC sample

increased a little after 30 FT cycles, comparing to the 3-day strength. Furthermore, the strength can increase continually when MPSC samples were set in normal condition after the FT cycles. This shows that the microstructure of MPC mortar was not damaged also after 30 FT cycles.

The resistance of concrete to freezing and thawing mainly depends on its degree of saturation and the pore system of the hardened cement paste. If concrete is never going to be saturated, there is no danger of damage from freezing and thawing. Even in a water cured specimen, not all residual space is water-filled and indeed this is why such a specimen does not fail on first freezing. Space available for expelled water must be close enough to the cavity in which ice is being formed, and this is the basis of air entrainment: if the hardened cement paste is subdivided into sufficiently thin layers by air bubbles, it has no critical saturation.

When the dilating pressure in the concrete exceeds its tensile strength, damage occurs. The extent of the damage varies from surface scaling to complete disintegration as ice is formed, starting at the exposed surface of the concrete and progressing through its depth. Each cycle of freezing causes a migration of water to locations where it can freeze. These locations include fine cracks, which become enlarged by the pressure of the ice and remain enlarged during thawing when they become filled with water. Subsequent freezing repeats the development of pressure and its consequences. When salts are used for deicing road or bridge surface, some of these salts become absorbed by the upper part of the concrete. This produces a high osmotic pressure, with a consequent movement of water toward the coldest zone where freezing takes place, which aggravates the scaling condition of concrete.

The reason of MPSC mortar possesses higher deicer scaling resistance than PC mortar can be attributed two aspects. First is less water inside the former than in the latter. Usually, the water to binder ratio of MPSC mortar was around 0.20, but for portland cement mortar it was around 0.44. Therefore, the former has denser microstructure than the latter. MIP test result indicates that the total porosity of MPC paste is about 9 percent by volume, while the total porosity of PC paste is about 20 percent by volume. The second reason is that there are many closed pores inside the MPC paste, very like the entrained PC concrete. These closed pores can prohibit water permeates into the inner of MPC matrix. The specimens were far from saturation of water.

(2) Wet-dry cycles in fresh water and natural sea water

The compressive strengths were determined at the end of each following curing stages: (I) After the MPC mortar samples were formed 3 days; (II) They were immersed in fresh water (FW) and sea water (SW) respectively, under room temperature. One wet-dry cycle kept 24 hours, including 12 hours in air and immersing in water 12 hours. The samples were put in water and taken out manually every day during wet-dry cycle; (III) Then those samples were set in lab air for

another 30 days and test strength; (IV) After that, the samples were immersed in FW and SW for another 60 days, respectively.

Fig. 6 shows the strength development after wet-dry cycles in FA and SW. After 30 wet-dry cycles in FW and SW, the strength of MPC samples even increased a little. After then, the strengths of MPSC mortars recovered and continued increasing when set in lab air for another 30 days. However, when the MPSC samples were immersed in FA and SW for 60 days again, the strength reduced. The result shows that there is no inverse effect under the wet-dry cycle in FW or SW. However, the strength reduced some when they were immersed in water for a long time, though the deduction of strength was not larger 17.0%. MPCs were suitable utilized in the environments that are dry or wet-dry alternatively.

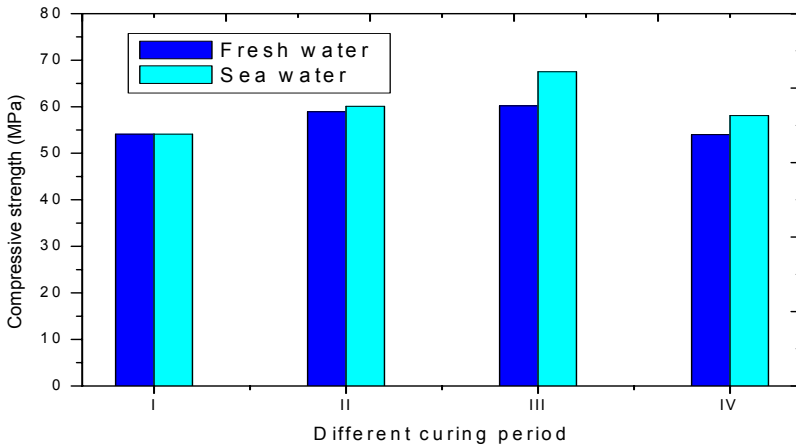


Fig. 6: Strength of MPC after wet-dry cycles in fresh water and sea water

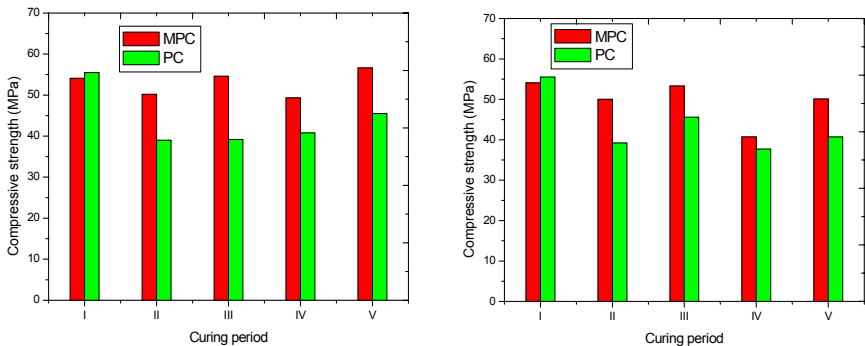
(3) Sulfate attack resistance test

The compressive strength was determined after each following stage: (I) After 3 days formed for MPC, 7 days for the PC mortar samples after they were molded, respectively; (II) The MPC mortars were immersed completely in solution of sodium sulfate (NS) and magnesium sulfate (MS) respectively, their concentration is 5 wt%. MPC mortars were immersed 30 days in the two solutions; (III) The same samples set in normal condition for another 30 days; (IV) Afterwards, all the mortars immersed in the corrosive solutions for 60 days; (V) At last, those specimens were set in lab air for 90 days.

After immersing 30 days in the NS solutions, comparing with the strength at 3 days, the strength of MPC sample increased. But, after 30 days immersed in solution of

MS₁ strength of CON decreased 7.2%. However, the strength loss of PC mortar is 29.4%; see Fig. 7.

After then, the corroded samples set in normal condition, the strengths of MPC mortar increase continually, and surpass their strengths at 3d. However, the strength of PC sample basically did not recover anymore. This indicated that the microstructure of MPSC can recover when separated from the attacking agents; however, the microstructure of PC had been damaged in the attacking agents. Then, these samples were immersed the sulfate solution again for another 30 day, respectively. The strength of MPC and PC decreased once more. However, after the specimens were put in lab air for another 90 days, the strength of MPC recovered much more (even catch up with the un-eroded specimens), the strength of PC mortar only recovered a little. From the results, it can be deduced that MPC sample has more resistance to NS attack than MS attack. In spite of which type of sulfate solution, MPC posses high salt attack resistance than PC mortar in the present research.



(a) After attacked in NS (b) After attacked in MS
Fig. 7: Strength development after attacked by sulfate solutions

4. Conclusions

Geopolymer is a type of amorphous aluminosilicate cementitious material. Geopolymer can be synthesized by polycondensation reaction of geopolymeric precursor, and alkali polysilicates. Comparing to portland cement, the production of geopolymers consume less energy and almost no CO₂ emission. Geopolymers are not only energy efficient and environment friendly, but also have a relative higher strength, excellent volume stability, better durability, good fire resistance, and easy manufacture process. Thus geopolymer will become one of the perspective sustainable cementitious materials in 21st century.

As a new sustainable cementitious materials, MPCs have much beneficial advantages in environments. Not only non-toxic wastes can be transferred into useful building materials, but also the toxic and/or radioactive waste can be solidified and stabilized safely with MPCs. Furthermore, MPC can incorporated with natural organic fibers to form composites, light weight or insulation materials. These natural organic fibers are not suitable bonding with portland cement. This is very meaning to the recycling of agricultural organic fibers in larger degree.

MPCs are high early strength and quick setting, very suitable to repair highways, airport runways, and bridges that are busy for transportation. The short waiting time for repairing means that saving lot of costs. In addition, MPCs have very good durability. Such as higher freezing-thawing and scaling resistance, low permeability, higher abrasion resistance, higher ability of sulfate attack resistance. MPCs are very suitable utilized in severe environments, such as frosty areas and corrosive conditions.

References

1. Mehta, P. K. Advanced cements in concrete technology, *Concrete International*, June 1999, 69-76.
2. J. Davidovits. "Geopolymers and geopolymeric new material." *Journal of Thermal Analysis* Vol. 35, 1998, 29-441.
3. J. Davidovits. Geopolymer chemistry and properties. *Proceedings of the First European Conference on Soft Mineralogy*, Vol.1, 1988, 25-48.
4. J. Davidovits. Recent progresses in concretes for nuclear waste and uranium waste containment. *Concrete International*, Vol.16, No. 12, 1994, 53-58.
5. J. Davidovits. High alkali cements for 21st century concretes. *Concrete Technology, Past, Present, and Future*, ed. P.K. Mehta, pp. 383-397, American Concrete Institute, Detroit ,SP-144, 1994.
6. R.E. Lyon, A Foden, P.N. Balaguru, M. Davidovits, and J. Davidovits. Fire-resistant Aluminosilicate Composites. *Journal Fire and Materials*, Vol. 21, 1997, 67-73.
7. J. Davidovits. Technical data sheet for geopolymeric cement type (Potassium, Calcium)-Poly(sialate-siloxo), *Proceedings of Geopolymere '99*, GEOCISTM, GLOBAL WARMING, NASTS award, 1994.
8. J. Davidovits. Properties of geopolymer cements. *Alkaline Cements and Concretes*, KIEV Ukraine, 1994, 9.
9. Kingery, W. D. Fundamental study of phosphate bonding in refractories: I, literature review. *Journal of the American ceramic society* 33(8), 1950, 239-50
10. Suguma, T., and Kukacka, L. E. Magnesium monophosphate cements derived from diammonium phosphate solutions. *Cement and concrete research* 13, 1987, 407-416.

11. Suguma, T., and Kukacka, L. E. Characteristics of magnesium polyphosphate cements derived from ammonium polyphosphate solutions. *Cement and Concrete Research* 13, 1987, 499-506.
12. Abdelrazig, B. E. I., and Sharp, J. H. A discussion of the papers on magnesia-phosphate cements. *Cement and Concrete Research* 15, 1985, 921-922.
13. Popovics, S; Rajendran, N., and Penko, M. Rapid hardening cements for repair of concrete. *ACI Materials Journal*, Jan-Feb. 1987, 64-73.
14. Abdelrazig, B.E. I, and Sharp, J. H. Phase changes on heating ammonium magnesium phosphate hydrates. *Thermochimica Acta* 129, 1988, 197-215.
15. Ramey, E. G., Moore, Raynond. K., Parker, Frazier. J.R., and Strickland, A. Mark. Laboratory evaluation of four rapid setting concrete patching materials. *Transportation Research Record* 1041, 47-52.
16. Abdelrazig, B.E. I., and Sharp, J. H., and El-Jazairi, B. The chemical composition of mortars made from magnesia-phosphate cement. *Cement and Concrete Research* 18, 1988, 415-425.
17. Yoshizake, Y; Ikeda, K; Yoshida, S; and Yoshizumi, A. Physicochemical study of magnesium-phosphate cement. *MRS Int'l. Mtg. On Adv.* Vol. 13, 1989, 27-38.
18. Abdelrazig, B.E. I., Sharp, J. H. and El-Jazairi, B. The microstructure and mechanical properties of mortars made from magnesia-phosphate cement. *Cement and Concrete Research* 19, 1989, 247-258.
19. Sarker, A. K. Phosphate cement-based fast-setting binders. *Ceramic Bulletin* 69(2), 1990, 234-238.
20. Sarker, A. K. Hydration/dehydration characteristics of struvite and dittmarite pertaining to magnesium ammonium phosphate cement systems. *Journal of Materials Science* 26, 1991, 2514-2518.
21. Seehra, S. S., Gupta, S. and Kumar, S. Rapid setting magnesium phosphate cement for quick repair of concrete pavements – characterization and durability aspects. *Cement and Concrete Research* 23, 1993, 254-266.
22. Bensted, J. A discussion of the paper “Rapid setting magnesium phosphate cement for quick repair of concrete pavements: characterization and durability aspects”. *Cement and Concrete Research* 24, 1994, 595-596.
23. Sarker, A. Investigation of reaction/bonding mechanisms in regular and retarded magnesium phosphate cement systems. *Cement Technology*, 1994, 281-288
24. Hall, David. A; and Stevens, Ronald. Effect of water content on the structure and mechanical properties of magnesia-phosphate cement mortar. *Journal of the American Ceramic Society* 81(6), 1998, 1550-56.
25. Yang, Quangbing, and Wu, Xueli. Factors influencing properties of phosphate cement-based binder for rapid repair of concrete. *Cement and Concrete Research* 29, 1999, 389-396.
26. Soudee, E., and Pera, J. Mechanism of setting reaction in magnesia-phosphate cements. *Cement and Concrete Research* 30, 2000, 315-321.

27. Yang, Quangbing, Zhu, Beirong, Zhang, shuqing, and Wu, Xueli. Properties and applications of magnesia-phosphate cement mortar for raped repair of concrete. *Cement and Concrete Research* 30, 2000, 1807-1813.
28. Jiang, H.Y., and Zhang, L. M. Research of magnesium phosphate cement. *Journal of Wuhan University of Technology* 23(1), 2001, 32-34.
29. Jiang, H. Y., Liang, B., and Zhang, L.M. Investigation of MPB with super early strength for repair of concrete. *Journal of Building Materials* 4(2), 2001, 196-198.
30. Hall, David. A, Stevens, R., and El-Jazairi, B. The effect of retarders on the microstructure and mechanical properties of magnesia-phosphate cement mortar. *Cement and Concrete Research* 31, 2001, 455-465.
31. Soudee, E., and Pera, J. Influence of magnesia surface on the setting time of magnesia-phosphate cement. *Cement and Concrete Research* 32, 2002, 153-157.
32. Yang, Quangbing, Zhang, Shuqing, and Wu Xueli. Deicer- scaling resistance of phosphate cement-based binder for rapid repair of concrete. *Cement and Concrete Research* 32, 2002, 165-168.
33. Singh, D., Wagh, A., Cunnane, J., and Mayberry, J. Chemically Bonded Phosphate Ceramics for Low-Level Mixed-Waste Stabilization. *J. Environ. Sci. Health*, A32(2), 1997, 527-541.
34. Wagh, A., Strain, R., Jeong, S., Reed, D., Krouse T., and Singh, D. Stabilization of Rocky Flats Pu-Contaminated Ash within Chemically Bonded Phosphate Ceramics, *J. Nucl. Mat.*, 265, 1999, 295-307.
35. J. Davidovits. Geopolymer cement to minimize carbon-dioxide greenhouse-warming. *Ceramic Transactions*, Vol. 37, 1993, pp.165-182.
36. J. Davidovits. 'Gopolymers: Inorganic polymeric new materials'. *Journal of Materials Education*, Vol.16, 1994, 91-139.
37. J. Davidovits, Douglas C. Comrie, John H. Paterson, and Douglas J. Ritcey. Geopolymeric concretes for environmental protection. *Concrete International: Design & Construction*, Vol.12, No.7, July 1990, pp. 30-40.
38. J.G.S. Van Jaarsveld, and J.S.J. Van Deventer. The effect of metal contaminants on the formation and properties of waste-based geopolymers. *Cement and Concrete Research*. 29, 1999, 1189-1200.
39. J.G.S. Van Jaarsveld, J.S.J. Van Deventer, and L. Lorenzen. Factors affecting the immobilization of metals in geopolymerized fly ash. *Metallurgical and Materials Transactions B*. Vol. 29B, Feb. 1998, 283-291.
40. J.G.S. Van Jaarsveld, J.S.J. Van Deventer. The potential use of geopolymeric materials to immobilize toxic metals: Part I. Theory and Applications. *Minerals Engineering*, Vol. 10, No. 7, 1997, 659-669.
41. J.G.S. Van Jaarsveld, J.S.J. Van Deventer, and A. Schwartzman. The potential use of geopolymeric materials to immobilize toxic metals: Part II. Material and Leaching Characteristics. *Minerals Engineering*, Vol. 12, No. 1, 1999, 75-91.

42. European R&D project BRITE-EURAM BE-7355-93: Cost-effective Geopolymeric cement for innocuous stabilization of toxic elements (GEOCISTEM). Final Report, April 1997.
43. Comrie Preliminary examination of the potential of geopolymers for use in mine tailings management, D. Comrie Consulting Ltd., Mississauga, Ontario, Canada, 1988.
44. Lyon, R.E. Technical Report DOT/FAA/CT-94/60, 1994.
45. J. Davidovits, and M. Morris. *The pyramids: An enigma solved*, Hippocrene Books, Inc., New York, 1988.
46. J. Davidovits. Ancient and modern concretes: what is the real difference? *Concrete International: Design & Construction*, Vol.9, No. 12, Dec. 1987, pp. 23-35.
47. Margie Morris. The cast-in-place theory of pyramid construction. *Concrete International: Design & Construction*, Vol.13, No. 8, 1991, pp. 29, 39-44.
48. Margie Morris. Archaeology and technology. *Concrete International: Design & Construction*, Vol. 9, No.12, Dec.1987, pp. 29-35.
49. Campbell D.H., and Folk R.L. The ancient pyramids—concrete or rock. *Concrete International: Design & Construction*, Vol.13, No.8, 1991, pp. 28-39.
50. J. Davidovits. Great pyramids debate. *Concrete International*, Vol. 14, No.2, 1992, 17-18.
51. M. Morris. Geopolymeric pyramids—A rebutal to Folk R.L., Campbell D.H. *Journal of Geological Education*, Vol.40, 1992, 28-39 and 344-346.
52. Folk R.L., and Campbell D.H. Are the pyramids built of poured concrete blocks? *Journal of Geological Education*, Vol.40, 1992, 25-34 and 344.
53. Harrell, J.A., and Penrod B.E. The great pyramid debate –Evidence from the Lauer sample. *Journal of Geological Education*, Vol.41, 1993, 358-363.
54. Mckinney R.G. Comments on the work of Harrell and Penrod. *Journal of Geological Education*, Vol.41, 1993, p. 369.
55. M. Morris. How not to analyze pyramid stone. *Journal of Geological Education*, Vol.41, 1993, pp. 364-369.