Recent Development of Geopolymers from Viewpoint of Carbon Dioxide Emission and Waste Management Problems

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Recent trends of geopolymers have been reviewed, referring to carbon dioxide emission and waste management problems closely rerated to COP3 and London protocol issued in 1996 and 1995, respectively. Geopolymer binders, simply called geopolymers, are based on polycondensation of [SO_4]-complexes to yield sodalite cage structures, different from Portland cements based on clinker mineral hydrations to yield insoluble hydrates. Metakaolin—potassium silicate solution or coal fly ash—sodium silicate solution system is conveniently used. Such ingredient mineral powders are called filler corresponding to powdered clinkers consisting of Portland cement binders simply called Portland cements. Flooding the alkali-silicate solutions to the filler, some Al^{3+} as well as Si^{4+} ions begin to dissolve and polycondensed [SiO_4]-polymers form bridged with Al^{3+} as well as Si^{4+} ions. Thus, solidified monolithic bodies can be obtained by the polycondensation of matrices. Geopolymers are fire-proof up to $1000°C$ as well as light weight, bulk density ~1.5 g/cm^3. Specifically, metakaolin based geopolymers are applicable to vehicles, replacing organic polymers even to aircrafts. Geopolymers are sulfate resistant and applications to sewage pipes as well as marine constructions are expected in a form of concrete made from coal fly ash and aggregate materials.

Keywords: Geopolymer, Filler, Carbon dioxide, Coal fly ash, Wastes

1. INTRODUCTION

The 21st century is called "the age of environment". Now we are faced with serious waste problems as well as the rapid growth of world population of mankind that may cause a shortage of drinking water and increasing carbon dioxide concentration in air. If the shortage of drinking water takes place, the population may decrease so that the carbon dioxide concentration in air may decrease eventually. However, as an urgent problem, the carbon dioxide concentration in air is on gradual increase so that realizing COP3 target, 6% cut of CO_2 emission, is almost on dead rock due to unexpectedly high rate of increasing CO_2 as seen in Fig. 1 [1].

At the time of industrial revolution evolved in the middle of 18th century the CO_2 concentration is believed to be on 280 ppm level. Since then, the concentration in air increased gradually to 310 ppm level, that is 30 ppm increase for 200 years (0.15 ppm/year in average rate). After World War II,

however, industrial development based on much consumption of natural resources evolved world over since around 1950 till to date so that rapid increasing CO_2 has been observed as seen in Fig. 1, i.e., 315 ppm level in 1960 and 365 ppm level in 2000. That is 50 ppm increase within only 40 years (1.25 ppm/year in average rate) and the increase is still going on rapidly even at this moment.

As indicated in Fig. 1 three categories of CO_2 sink are considered. They are oceans, forests and atmosphere. The sink capacities of oceans and forests are nearly constant and limited. Consequently, it is quite natural that excess CO_2 should accumulate in the atmosphere causing green house effect. Actually, the temperature of air on the earth is steadily increasing year by year as seen in Fig. 1 and the period from 1990 to 2000 is called "hottest 10 years" in the last 1000 years.

World CO_2 emission shares are represented in Fig. 2 [2] according to countries. Although world CO_2 emission is
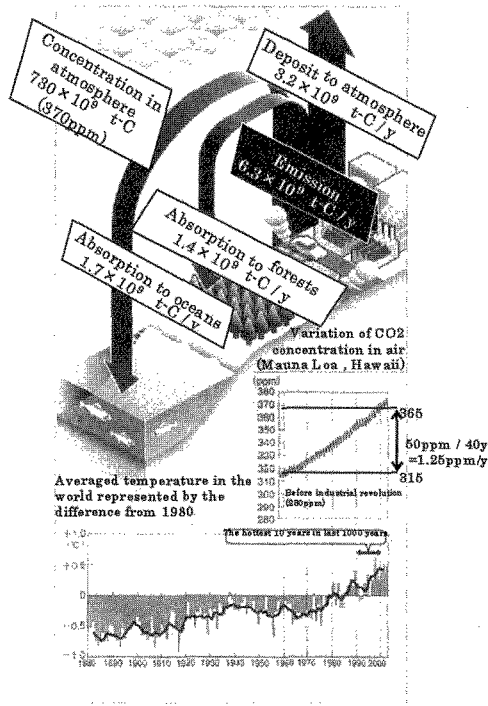
Fig. 1. Source and sink of CO_2 emission and imbalance between them causing green house effect.

estimated 6.3 billion tons as C at the moment, it was 6.2 billion tons as C in 1994. The share of Japan in 1994 was 4.9% which nearly corresponds to the world CO_2 emission of Portland cement industries, that was 5% in 1988. However, at the moment the CO_2 emission of Portland cement industries is estimated to reach 7 % corresponding to nearly the share of Russia due to increasing production of Portland cements specifically in developing countries including China. It is well-known that 1 ton production of Portland cements releases 1 ton CO_2 due to consuming mainly limestones as CaO source. Limestones are composed of very high quantity of $CaCO_3$ that can be regarded as "fossil of CO_2" consisted of the atmosphere of the earth date back to geologic time.
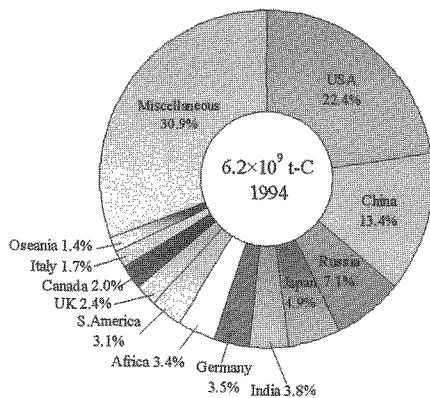

Fig. 2. World CO_2 emission and shares of countries.

As seen in Fig.3 [3], replacing Portland cements with geopolymers, which are also called "calcium-free cements", may be a strong countermeasure for suppressing CO_2 emission, since geopolymer process emits only 20% CO_2 compared with Portland cement process. That is to say, 80% CO_2 reduction will be realized, if Portland cements are thoroughly replaced with geopolymers as an extreme case. Suppose that present Portland cement production is frozen at the time of 1990, the amount of excess CO_2 emission due to world Portland cement production after 1990 can be reduced. Thus, the CO_2 level caused by Portland cement productions can be maintained almost flat by replacing a part of Portland cements with
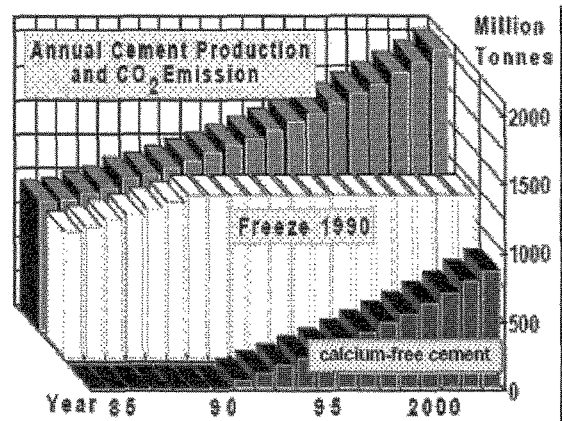

Fig. 3. Effective CO_2 emission reduction after replacing geopolymers for Portland cements, if frozend by the year 1990. Multiply 12/44 to convert CO_2 as C.

calcium-free cements, that is geopolymers which can be solidified at ambient temperature as well as at steam curing temperatures, 60-80℃.

On the other hand, we are faced with serious waste problems due to high activity of modern industries as well as modern luxurious way of life style. As seen in Fig.4 [4], emission of industrial wastes was 4.1 billion tons in Japan in 2003. Although nearly the half is recycled nowadays, the rest half is discarded to final dumping sites including open seas. There are some open sea areas for dumping around Japan as indicated in Fig. 5 [5]. Wastes such as slimes including mining wastes and animal manures have mainly been discarded to the open seas in Japan. However, London protocol issued in 1995 prohibits such discarding in order to maintain ocean clean. This may be a serious problem to the confined countries such as Japan. Therefore, much more advancement of recycling is requested at the moment. The geopolymer technique can also contribute to London protocol to make concrete-like monolithic bodies from waste inorganic slimes as filler of geopolymers.
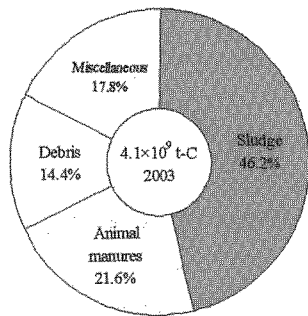
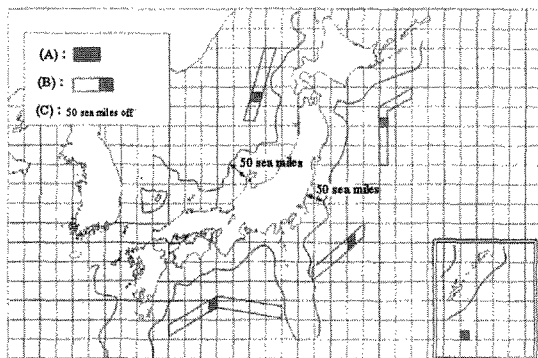Fig. 4. Annual discharge and shares of wastes in Japan.

Fig. 5. Specific dumping spots of wastes around Japan.

(A) Sand and slime including hazardous metals etc.

(B) Inorganic slime including mining wastes etc.

(C) Organic slime including sewage wastes etc.

Fig. 6. Elution properties of calcined kaolin. $\triangle$ and $\diamondsuit$ showing Al^{3+} at 25°C and 80°C, respectively. ● and ■ showing Si^{4+} at 25°C and 80°C, respectively.

Fig. 7. Elution of various kinds of coal fly ash vs NaOH concentration.

2. GEOPOLYMERS VERSUS PORTLAND CEMENTS

Geopolymers dating back to Josef Davidovits's patent in 1982 [6] require two basic raw materials called "filler" and "geopolymer liquor", corresponding to powdered cement and water of Portland cement system, respectively. The filler is further classified into two categories, active filler and inactive filler. Metakolin and coal fly ash are typical active fillers having relatively high elution to alkaline solutions on which intensive studies have been made recently as shown in Figs 6 and 7 [7,8]. To the contrary, quartz and hematite are typical inactive fillers having less elution to alkaline water.

The geopolymer liquor consists of alkali-silicates so called water glass dissolved in water. Currently, two series of water glass are commercially produced, i.e., K-series and Na-series. In 1990s K-series were mainly studied in combination with metakaolin. Although K-series exhibits superior mechanical strength to that of Na-series, kaolin resources are unevenly distributed in the world. Furthermore, K-series water glass is considerably expensive. Therefore, with the advent of 2000s studies of Na-series in combination with coal fly ash began
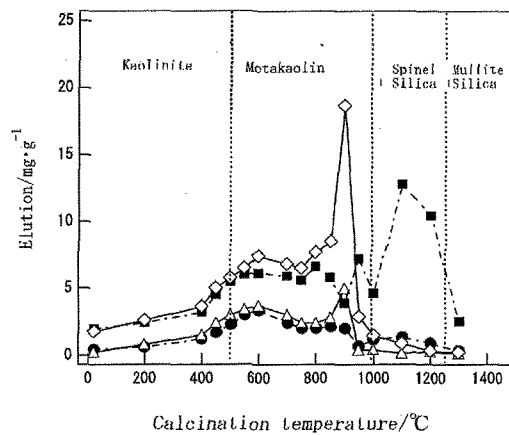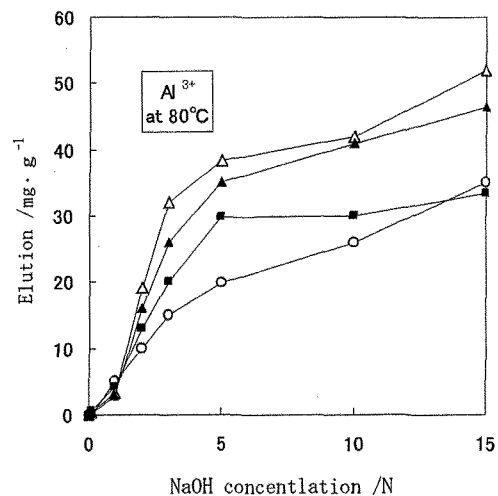
popular due to urgent waste management problems in the world, specifically wastes discharged from power plants, that is coal fly ash.

Although nowadays Portland cements have some varieties according to working objectives, this kind of cements dates back to the patent of Josef Aspdin in 1824 [9], improved and produced for more than 180 years. To manufacture Portland cements we have to burn so called clinkers firstly from calcareous resources mixing with argillaceous resources at elevated temperature, generally 1450-1500°C. Thus we obtain clinkers consisting of so called clinker minerals, C_3S, C_2S, C_3A and C_4AF as expressed in cement chemical notations (C=CaO, $S=SiO_2$, $A=Al_2O_3$ and $F=Fe_2O_3$). After pulverizing the clinkers added with a small amount of gypsum, we obtain powdered cements for shipping. When water is flooded, C_3S and C_2S

precipitate so called C-S-H gels and portlandite, $Ca(OH)_2$ by hydration. Formation of C-S-H gels is topochemical and this amorphous mineral grows on the surface of original C_3S and C_2S grains so that hydration proceeds not entirely, remaining unhydrated cores. Portlandite formation is not topochemical type but through-solution type so that this mineral precipitates apart from C_3S and C_2S grains. It is said that the ratio of C/S for C-S-H gels is ranging from 0.5 to 1.7, 1.3 in average [10]. As seen in Fig. 8, C-S-H gels form on the surface of C_3S and C_2S grains yielding chestnut-burr textures entangled each other. The hydration of C_3S and C_2S grains is a main course of hydration and this entangling leads to coagulation which plays a major role of exhibiting very strong mechanical strength of cementitious bodies of Portland cements.
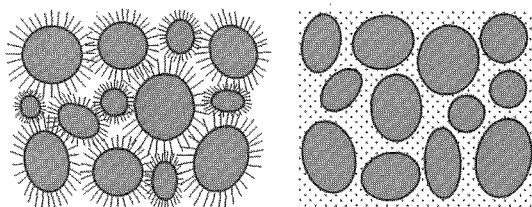

Fig. 8.   Schematic and simplified textures of hydrated Portland cements (left) and Geopolymers (right).

The subordinate hydration courses are C_3A and C_4AF hydrations. C_3A grains have very high solubility to water. As soon as flooding, this mineral dissolves and precipitates hydrates causing flash setting. To prevent the flash setting, very small amount of gypsum is premixed. Therefore, C_3A gives rise to famous acicular crystals of ettringite, $C_6A\bar{S}_3H_{32}$ mildly, reacting with dissolved gypsum component generally accompanied with platy crystals of Ca-monosulphate hydrate, $C_4A\bar{S}H_{32}$ ($\bar{S}=SO_3$ and $H=H_2O$). After consuming the gypsum component, C_3A gives rise to generally C_4AH_{19} and C_2AH_8 to dissolve completely, since C_3A hydration is through-solution type. C_4AF is not so active and the quantity in cements is very small and can be neglected, yielding Fe-bearing gel hydrates in extremely later age.

The mechanism of hardening of geopolymer is quite different from the hardening of Portland cements, since
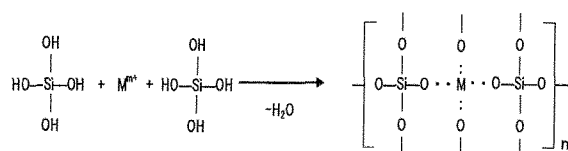
principle of geopolymer is not based on hydration but on polymerization. As seen in Fig. 9, silicon ions are present in a coordination state of $[Si(OH)_4]$ complexes and alkalis are liberated in water glass solution. The complexes can be polymerized through polycondensation, but generally it takes long time in alkaline conditions. However, if foreign metallic ions are present together, the polycondensation proceeds relatively fast to yield metal-bearing silicate polymers so called "geopolymers". Similar phenomena are widely observed in terrestrial materials called sedimentary rocks due to the action of rain falls.

In practical geopolymer system the foreign metallic ions are supplied from the filler so called the active filler as illustrated in Fig. 10. The elution of the filler should be adequately mild. Otherwise the filler mix cannot be handled due to flash setting. If the elution is too low as represented by the inactive filler, the filler mix cannot be solidified. In such a case active filler should be mixed in appropriate amounts [11]. Consequently, the texture of geopolymer bodies is not complicated as seen in Fig. 8 in which remaining filler grains are simply embedded in the polymerized matrices of amorphous gels.
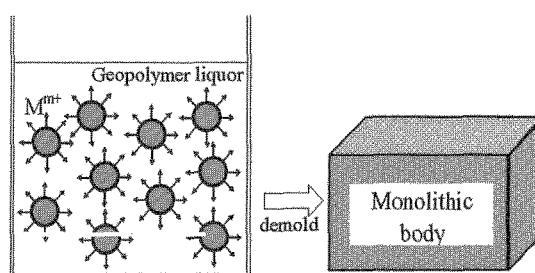

Fig. 10.   Schematic illustration of dissolution of filler and a solidified body obtained after demolding.

It is generally said that the polymerized silicate gels composed of the matrices yield sodalite cage structures, generally consisting of 3D-hexagonal rings as seen in Fig. 11 [3]. Alkalis as well as water molecules are trapped in the cages. Specifically, alkalis are incorporated into the structure for charge compensation balancing with Al^{3+} ions which replace
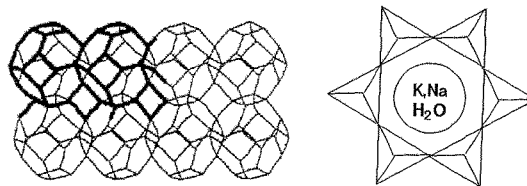

Fig. 11.   Sodalite cage structures and trapping of alkalis as well as water molecules inside the cages.

Fig. 9.   Polycondensation of $[Si(OH)_4]$-complexes bridging with metals.

tetrahedral Si^{4+} ions as typically seen in feldspar structures as represented by $KAlSi_3O_8$-$NaAlSi_3O_8$ system. Strictly saying, feldspathoid structures are preferable due to presence of much alkalis in geopolymers. Some researchers estimate zeolite structures instead of sodalite structures [12, 13]. The replacement of Al^{3+} for Si^{4+} is well studied in literatures [14, 15] as seen in Figs. 12 and 13 in which a mirror image behavior between Al^{3+} and Si^{4+} ions is clearly seen. Moreover, it was found that the alkali contents increased with increasing pH.
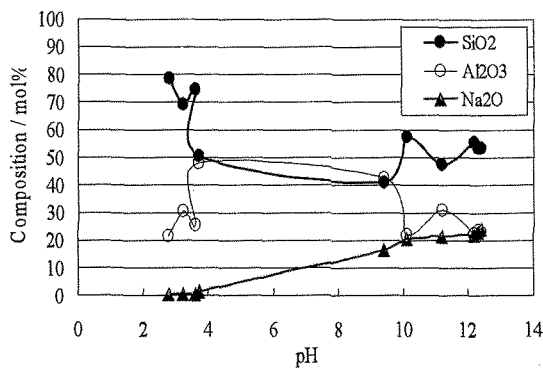

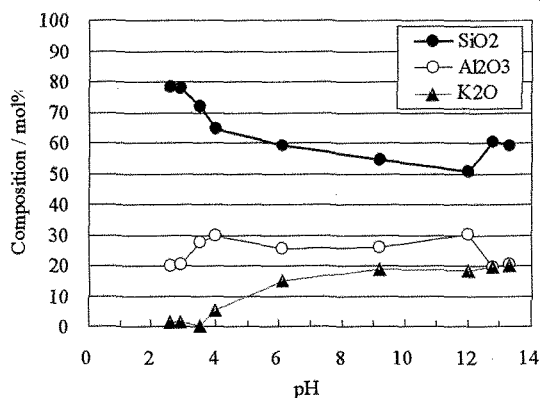Fig. 12. Variation of chemical compositions of Na-bearing silicate gels against pH.

Fig. 13. Variation of chemical compositions of K-bearing silicate gels against pH.

3. PRESENT AND FUTURE OF GEOPOLYMERS

Other than what was stated in the section of introduction, geopolymers have several peculiar characteristics, compared with Portland cements.

Firstly, geopolymers are fire-proof and light weight. The bulk densities of geopolymer matrices are around $1.5g/cm^3$. It is said that geopolymers are durable up to $1000°C$, while Portland cements up to $400°C$. The most preferable applications of these properties may be to ships as well as vehicles including subway trains. Actually, a ferry boat installed with decoration panels made from metakaolin is already in service in Finland. Racing cars equipped with fire-proof bodies appeared already hybridized with carbon fibers, even applicable to aircrafts.

Secondly, geopolymers are sulfate resistant. The most fascinating application of this property is sewage pipes which are damaged by the action of sulfur bacteria producing sulfuric acid in the pipes specifically in urban areas where so frequent collapse beneath streets are reported due to heavy traffics so that much budget is lost for repairing every year, since Portland cement pipes so called Hume pipes are not resistant to sulfates as well as sulfuric acid. Furthermore, marine constructions are another way of applications to make use of the highly resistant property to sulfates. Sea shore banks as well as fish reefs are preferable and such marine developments have an advantage on the waste managements as well, since oceans occupy boundless areas so that tremendous amounts of waste can be discarded in the form of geopolymer concretes consisting of geopolymer matrices and aggregates like Portland cement concretes currently applied in practice so widely. An example of sewage pipe is shown in Fig. 14. A sliced geopolymer concrete is shown in Fig. 15, having 50MPa compressive strength.
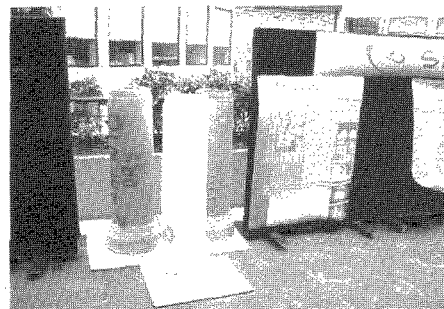

Fig. 14. Sewage pipes made from geopolymers exhibited in Geopolymers 2002 conference held in Melbourne.
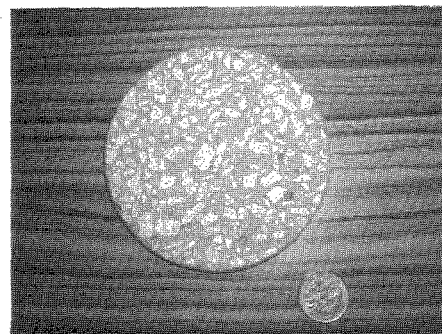

Fig. 15. A piece of sliced geopolymer concrete.

Thirdly, as shown in Fig. 16 some geopolymer monoliths consist of nano-scale pores, which facilitate moisture absorption and desorption according to Kelvin's capillary condensation equation. To maintain in-door humidity in a range between 40%RH to 70%RH requires 3.2 nm to 7.4nm pores in diameter and this condition is satisfied with some geopolymer monoliths made from PFBC ash (a different kind of coal ash rich in Ca-component as well as SO_3-component) blended with ordinary coal fly ash [16]. Accordingly, application of this kind of material to rooms can contribute to saving air conditioning energy, especially in humid Japanese summertime, leading to suppression of carbon dioxide emission from power plants at last.
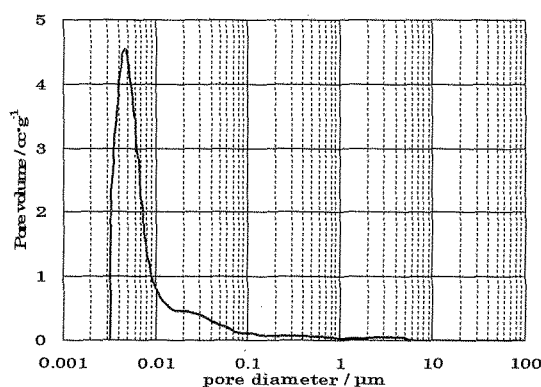

Fig. 16.   Nano-scale pore size distribution of special-made geopolymers solidified at room temperature.

Finally, the definition of geopolymers should be mentioned. There are two extreme categories of Portland cement binders and geopolymer binders as seen in Fig. 17. The former is based on hydration of clinker minerals to produce insoluble minerals so called hydrates, while the latter is based on polymerization of [SiO₄]-complexes bridged with metallic ions such as Al^{3+} to yield sodalite cages. Alkalis are trapped inside the cages, if water glass solutions are used as monomer source. On the other hand, there is another category of cementitious binders called "alkali activation cements" which partially encompass Portland cements and geopolymers as represented in Fig. 17. There are some confusions hitherto between alkali activated cements and geopolymers. To solve these controversial nomenclatures, the authors would like to stress that genuine geopolymers should be calcium-free in order to avoid the confusions.

The geopolymer binders are going to widen their applications in high rate world over to contribute to solving current urgent problems, that is, high rate increase of carbon dioxide emissions and waste management problems in
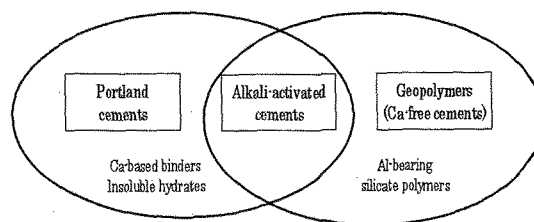

Fig. 17.   Positioning of geopolymers in the two extrems of binders.

industries. Specifically, introduction of the geopolymer technique to the infrastructures of developing countries would be of great significance, since the current world increasing productions of Portland cements are mostly due to the extending infrastructures in developing countries. Eventually, geopolymers might greatly contribute to prevention of green house effect occurring due to the excess CO_2 release into the atmosphere.

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