Environmentally Driven Geopolymer Cement Applications.

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Summary:

Environmentally driven geopolymer applications are based on the implementation of (K,Ca)-Poly(sialate-siloxo) / (K,Ca)-Poly(sialate-disiloxo) cements. In industrialized countries (Western countries) emphasis is put on toxic waste (heavy metals) and radioactive waste safe containment. On the opposite, in emerging countries, the applications relate to sustainable development, essentially geopolymeric cements with very low CO2 emission. Both fields of application are strongly dependent on politically driven decisions.

a) Heavy metals waste encapsulation:
This application started in 1987, in Canada, with the financial support of CANMET Ottawa, Ontario Research Foundation, Toronto, and Comrie Consulting. It was dedicated to the stabilization of based metal mine tailings. Laboratory results were excellent, yet the experimentation stopped because of lack of political support.

b) Uranium mine tailings and radioactive sludge:
Started in 1994 within the research project GEOCISTEM, funded by the European Union. The GEOCISTEM project was aimed at manufacturing cost-effectively new geopolymeric cements. It was experimented on two important uranium-mining locations of WISMUT, former East Germany, with the collaboration of BPS Engineering. Germany. First on sludges containing radionuclides, toxic heavy metals and hydro-carbons. Then, a pilot experimentation totalizing 30 tons of low-level radioactive waste was run in 1998 at the WISMUT's Schlema-Alberod water treatment plant. The geopolymer technology gives a monolithic product, which can be easily handled, stored and monitored. It requires only simple mixing and molding technology known from conventional solidification methods. Our results clearly show that solidification with Geopolymeric Cement (K,Ca)-Poly(sialate-siloxo) is a prime candidate to fill cost-efficiently the gap between conventional concrete technology and vitrification methods. Due to the reduced effort to prepare, operate and close the landfill, geopolymeric solidification leads to approximately the same unit cost as by conventional Portland cement, but provides in most aspects the performance of vitrification.

c) Green-House CO2 mitigation, low CO2 geopolymer cements:
Started in 1990 at PennState University, Materials Research Laboratory, USA, and continued within the frame of the European Project GEOCISTEM. In 2002, it has been declared technological priority by the China's government. The production of 1 tone of Geopolymeric cement generates **0.180 tones of** CO2, from combustion carbon-fuel, compared with 1.00 tones of CO2 for Portland cement. Geopolymeric cement generates **six (6) times less** CO2 during manufacture than Portland cement. This simply means that, in newly industrializing countries, six (6) times more cement for infrastructure and building applications might be manufactured, for the same emission of green house gas CO2.

A) Heavy metals waste encapsulation (1987)

Zeolitic materials are known for their abilities to adsorb toxic chemical wastes. Geopolymers behave similarly to zeolites and feldspathoids. They immobilize hazardous elemental wastes within the geopolymeric matrix, as well as act as a binder to convert semi-solid waste into an adhesive solid. Hazardous elements present in waste materials mixed with geopolymer compounds are «locked» into the three dimensional framework of the geopolymeric/zeolitic matrix. Geopolymeric cements designed for waste containment provide early-high strength development which can be enhanced with the adjunction of microwave preheating devices aimed at raising the inside temperature of the waste form up to 30-35°C. Following curing at room temperature yields solid, monolithic, high-strength (100 MPa compressive strength) Geopolymer waste forms. Ambient temperature processing of Geopolymer based waste forms deals essentially with the safe and innocuous disposal of toxic and hazardous wastes and mine tailings. The method involves producing and innocuous material with improved strength and acid resistance. Many of the contaminated soils contain both inorganic and organic toxic compounds. For wastes with both of these hazards (mixed-wastes), in situ immobilization offers the one-step treatment advantages of speed and economy. Without any treatment, such hazardous materials require a special landfill with double plastic-and-clay liners and leachate collection systems. These lined hazardous waste landfills are difficult and expensive to install. Also, they require long-term monitoring (30 years) and show high rates of failure in the first decade. On the other hand, geopolymer monoliths are easier to install and are maintenance free. Monitoring becomes inconsequential because the geopolymeric materials conduct no measurable amounts of water (Table.1).

Table 1: Permeability values in cm/s:

sand	10^{-1}
clay	10^{-7}
granite	10^{-10}
Fly Ash cement	10^{-6}
Portland cement	10^{-10}
Geopolymer cement	10^{-9}

Also, the binding matrices control the maximum credible concentrations of hazards in the leachate and keep them below known health effect levels. In addition, geopolymer monoliths can hold the hazards below the detection limits of analytical methods.

Immobilization technologies with geopolymeric materials have three goals.

The first goal is to seal the hazardous materials into an impermeable monolith. This prevents the direct contact of potential leachates, like ground water and percolating rain. Conventional cheap inorganic binders, soluble silicate based, Portland cement based, fly-ash-lime based, are unsuited for solidification of various industrial wastes, particularly those containing:

- sodium salts of arsenate, borate, phosphate, iodate and sulphides;
- salts of magnesium, tin, zinc, copper, lead.

Conventional inorganic binders are also unsuited for solidification of end-product residues with high sulphide contents. These mineral and organo-metallic wastes generate sulphuric acid, which leaches out heavy metals. Unlike conventional Portland cement, geopolymeric cements do not rely on lime and are not dissolved by acidic solutions. Portland based cements (plain and slag blended) are destroyed in acidic environment. Calcium aluminate cement is expensive to produce, and does not behave satisfactorily, having 30 to 60% of weight loss (destruction). Geopolymeric cements, Potassium-Poly(sialate-siloxo) type, Geopolymite®, remain stable with a loss in the 5-8 % range.

The second goal is to design a solid matrix that binds the specific hazardous elements. This reduces the mobility of the hazards within the monoliths. A research program on toxic waste stabilization was funded by CANMET Canada (1988) (Canada Centre for Mineral and Energy Technology). Fig.1 displays examples of the results obtained at Ontario Research Foundation (Canada) on the innocuous solidification and stabilization of non-metallic and uranium mining tailings. These testing procedures, used in the fundamental research program were conducted in accordance with the Government of Ontario Ministry of Environment regulatory standards (Regulation 309); they represent “worst case” scenarios. Reg. 309 specifies that the solid is pulverized in order to expose a maximum surface area to the acidic solutions, and leached in solutions of acetic acid, 24 hours at constant pH 5, which represents an environment far more harsh than any which will be encountered in natural conditions.

The pollutants have become locked into the three dimensional geopolymeric-zeolitic framework. Acid-resistant geopolymeric containment has been shown to greatly minimize the leaching of iron, cobalt, cadmium, nickel, zinc, lead, arsenic, radium and uranium (Fig. 1).

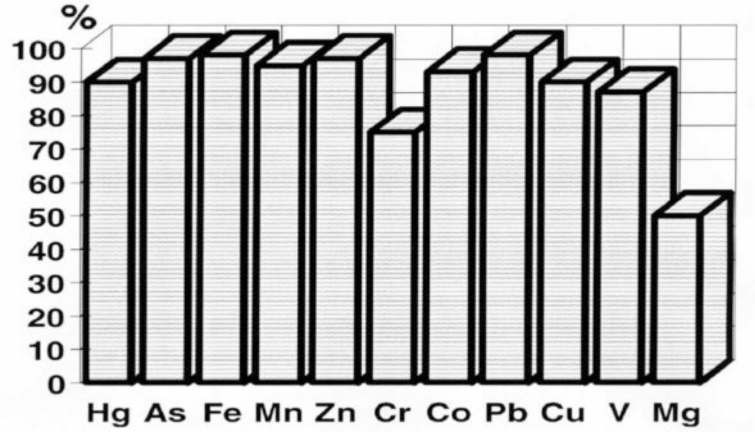

Figure 1!: Amount of hazardous elements locked in the geopolymeric matrix.

The third goal is to make a durable monolith that weathers environmental stresses. Using ancient building materials from Rome and earlier civilizations as models, we are able to formulate durable, impermeable monoliths, which will endure at least 2,500 to 5,000 years of weathering. In the types of consolidation known in the prior art, the hazardous waste is agglomerated with Portland cement or silicate binders or lime blended fly ashes, and it is assumed that the matrix will not deteriorate. Yet, comparative studies of restorations performed on archaeological buildings dating from the Roman time show that modern Portland cement is strongly affected by aggressive climatic conditions and does not last more than 50 years, whereas Roman mortars are unaffected, even after more than 2000 years. Our studies performed at the Institute for Applied Archaeological Sciences, Barry University, Florida, USA, have demonstrated that the pozzolanic formulation used by the Romans, involved a geopolymeric setting, yielding zeolitic material. Older mortars were studied, such as the lime mortars of Jericho and Tell-Ramad, dating as far as 7000 BC, and which contain up to 40% by weight of analcime zeolite. Ancient concretes and mortars demonstrate the exceptional durability of zeolitic cements, analogous to synthetic geopolymers discussed here, and are indicative of the erosion resistance, which can be expected of modern geopolymeric cements.

B) Uranium mine tailings and radioactive sludge

Results from the European Research Project GEOCISTEM (1994-1997)

Project funded by the European Commission, BRITE-EURAM BE-7355-93.

The first research has tested the basic properties of concretes elaborated with local polluted aggregates on a WISMUT's uranium mining site, in Ronneburg, Thüringen. Designed materials and technology could be applied later to borehole plugging, shaft sealing, geological barriers, cappings, dams and walls, for cleanup uranium mine tailings. All the tests have been carried out with a geopolymer cement from type PZ-GEOPOLY®, (K,Ca)-Poly(sialate-siloxo) cement and a synthetic «Ronneburg!» aggregate comprising 15% Kaolinite, 7% Pyrite and 5% Plastorit. These tests consisted of a series of tests on mortar bars in order to determine mechanical, physico-chemical properties and durability (chemical corrosion) in acidic medium, ph=2.8, after 28 days and 56 days in water bath and/or acid bath. These tests confirm the exceptional good properties of geopolymeric cements in chemically corrosive environments.

A second research dealt with acid-resistance study carried out on GEOCISTEM CARBUNCULUS Cement™ in comparison with Cement I.42.5 Portland (Cementi Buzzi). Metallic mine tailings usually generate sulfuric acid that results from the oxidation of pyrite. The resistance to strong sulfuric acid solution (5% H_2SO_4 solution) was investigated in two series of tests:

1) after only 24 hours of hardening in water: CARBUNCULUS cement remains intact whereas the acid corrosion has destroyed more than 50% of Cement I.42.5 (weight loss and change in shape and volume).
2) after the standard 28 days of hardening in water: CARBUNCULUS cement loses less than 5% after 56 days, whereas Cement I.42.5 is strongly affected by the acidic medium (-63% of weight loss after 56 days).

A third research project provided an inertization method for toxic liquid by absorption and subsequent encapsulation. It started with the study of the absorption capacity data for natural sorbents such as bentonites, zeolites and vermiculites, for removal of heavy metals, arsenic, radioactive elements from concentrated solutions, thermally treated mixed-wastes (organic-inorganic). Best results, with respect to absorption and encapsulation are obtained with Na-modified bentonites that absorb up to 850 g of liquid per 1 kg of bentonite. Pelletisation, coating and inertization are achieved with laboratory geopolymeric binders and the selected CARBUNCULUS cement. The results are compared with Portland cement coating. Laboratory geopolymeric binders, followed by CARBUNCULUS cement, with respect to attrition and leachate properties, provide the best results.

The project at WISMUT Uranium mining sites (former East-Germany) (1998-2000) (Fig.2)

Sludges containing radionuclides, toxic heavy metals and hydro-carbons were solidified with Geopolymeric Cement (K,Ca)-Poly(sialate-siloxo) providing excellent long-term structural, chemical and microbial stability, satisfying high standards of contaminant retention. The novel technology gives a monolithic product, which can be easily handled, stored and monitored. It requires only simple mixing and molding technology known from conventional solidification methods.

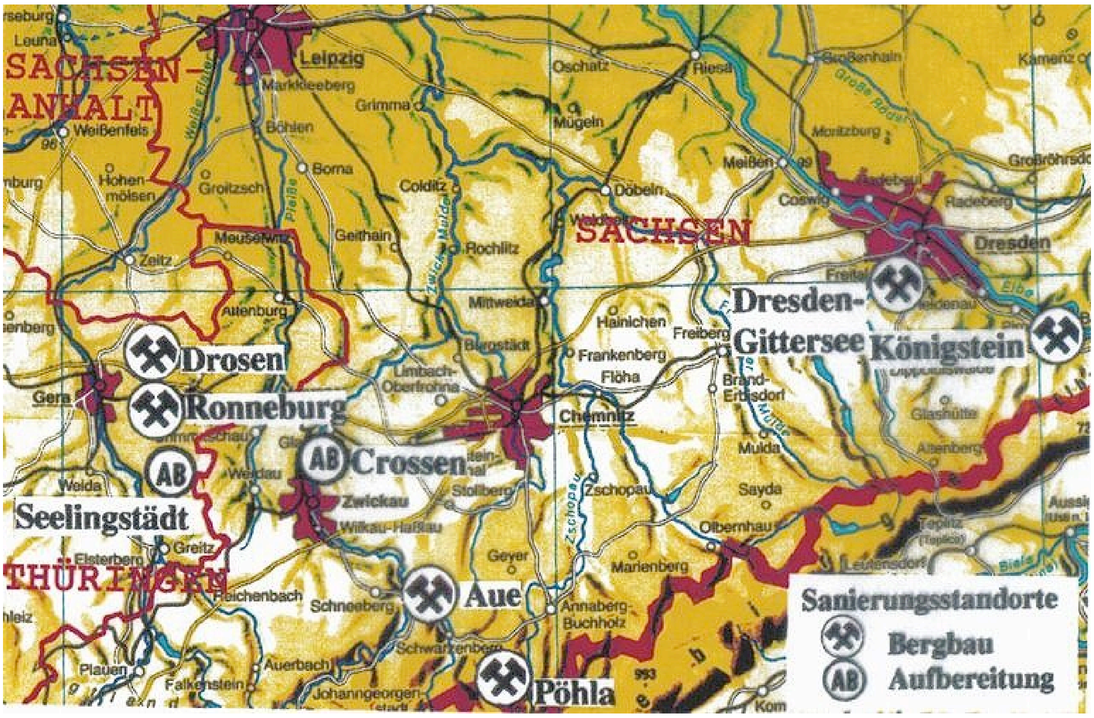

Figure 2!: Uranium mining sites of WISMUT in Germany

Extensive laboratory investigation has been carried out with the partnership of the German Engineering company, B.P.S. Engineering, Zwickau, to demonstrate the performance of the novel solidification method under adverse stress conditions. In particular, the sludges of a treatment facility for uranium mining effluents and sludges from a settling pond, contaminated organically, radioactively and by heavy metals, have been treated (Fig. 3). An optimized two-step technology, known as GEOPOLYTEC® was successfully adapted to the specific characteristics of these sludges. Moreover, the Geopolytec® process delivers excellent results for radioactive and arsenic-loaded sludges from municipal drinking water purification plants that are sensitive with respect to public risk perception and regulatory policy.

Figure 3!: Decantation pond at WISMUT Drosen site.

Pilot-scale experiments that show the method’s maturity for industrial use and to provide realistic material and operation cost estimates, were performed on uranium mine sludges. Several tons were solidified in WISMUT's Schlema-Alberoda water treatment plant in 1999 (Fig. 4). Our results clearly show that solidification with Geopolymeric Cement (K,Ca)-Poly(sialate-siloxo) is a prime candidate to fill cost-efficiently the gap between conventional concrete technology and vitrification methods. Due to the reduced effort to prepare, operate and close the landfill, solidification by Géopolymère® leads to approximately the same unit cost as by conventional Portland cement, but provides in most aspects the performance of vitrification (Fig. 5).

Figure 4!: The water treatment plant at AUE Schlema-Alberoda. The geopolymeric waste material was poured in big-bags, ready for disposal.

Figure 5!: Big-bags with the geopolymeric waste material and place of disposal.

Very promising results were obtained for the long-term stability and contaminant retention under several testing procedures. They shows that the GEOPOLYTEC® process is now mature for industrial application.

To sum up!: The GEOPOLYTEC ® process (geopolymeric cement) like vitrification, provides:

- high strength, acid resistance, long-term durability
- geological analogues (>10.000 years)
- archaeological analogues (>2.000 years)
- but uses simple cement like technology

C) Green-House CO2 mitigation, low CO2 geopolymer cements (1990)

The production of Geopolymeric cement does not require any calcination of calcium carbonate, unlike ordinary Portland cement (O.P.C.), which results from the calcination of limestone (calcium carbonate) and silico-aluminous material according to the reaction:

$$5CaCO_3 + 2SiO_2 \rightarrow (3CaO,SiO_2)(2CaO,SiO_2) + 5CO_2$$

The production of 1 tone of O.P.C. directly generates 0.55 tones of CO2 and requires the combustion of carbon-fuel to yield an additional 0.40 tones of CO2.

To simplify: 1 t of Portland cement = 1 t of CO2.

In contrast, Geopolymeric cement only requires the calcination at 800°C for two geological ingredients, Carbunculus and KANDOXI. High furnace slag is a by-product that no longer needs any subsequent treatment.

CO2 emission in manufacturing 1 tone geopolymeric CARBUNCULUS Cement ^{TM}

Ingredient	heat treatment	CO2/tonne of ingredient	CO2 ratio in 1 tone of cement
carbunculus	800°C	0.17 t	0.095 t
Kandoxi	750°C	0.15 t	0.035 t
Slag	-	-	-
K-silicate	1200°C	0.30 t	0.034 t
energy for grinding	-	-	0.020 t
Total, for 1 tone of Geopolymeric cement :			***0.184 t***

The production of 1 tone of Geopolymeric cement generates **0.184 tones of** CO2, from combustion carbon-fuel, compared with 1.00 tones of CO2 for Portland cement. Geopolymeric cement generates **5-6 times less** CO2 during manufacture than Portland cement. This simply means that, in newly industrializing countries, 5-6 times more cement for infrastructure and building applications might be manufactured, for the same emission of green house gas CO2. Development means building infrastructures and houses, in short, cement and concrete. The progress of any national economic development is judged by the growth rate of infrastructures, which is linked to the cement production. Due to the exponential use of concrete, cement production has increased at a much higher speed than atmospheric CO2 concentration, i.e. than all major CO2 emission caused by human activities, such as energy and transportation.

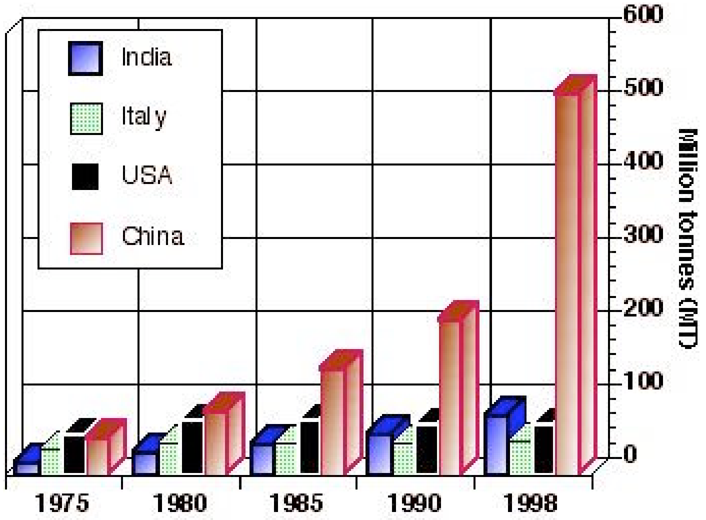

Figure 6!: CO2 emissions during Portland cement manufacture for countries and years.

As time goes by, Portland cement manufacture thus has a greater influence on the trends of CO2 emissions and the predicted values for atmospheric CO2 concentration should be corrected accordingly. In year the 1990 the world cement industry emitted 1,100 million tones of CO2, with China accounting alone for 210 million tones. 1998's statistics give China with 550 million tones (Fig. 6).

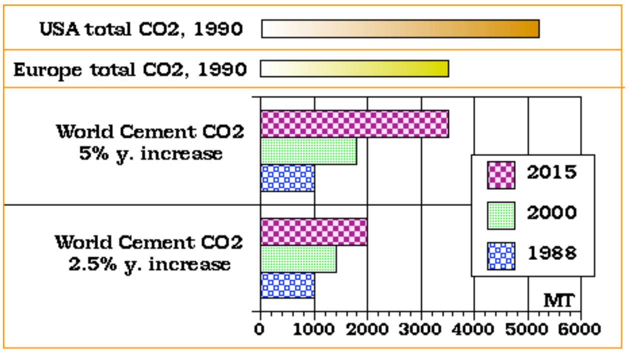

Figure 7!: Cement CO2 emission forecast for 2015

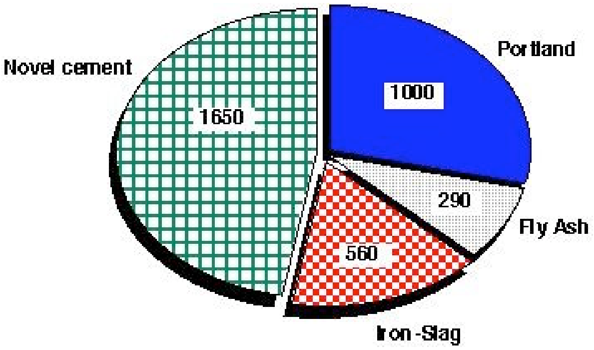

Figure 8!: Need for Novel cement in 2015

In the year 2015 (Fig. 7), world cement CO2 emissions could equal the 3,500 millions tones presently emitted by Europe (E.U.) human activities (industry + energy + transportation), or 65% of present total U.S. CO2 emission (present cement CO2 is only 50 million tones or 1.5% of total USA). This addresses the need for new technologies to be adapted to the economy of the developing countries (Fig. 8). Introducing low-CO2 Geopolymeric cements, not only for environmental uses, but also in construction and civil engineering, would reduce carbon-dioxide emission caused by the cement and concrete industries by 80%.

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