PPP 0024

APPLICATIONS OF GEOPOLYMER TECHNOLOGY TO WASTE STABILIZATION

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ABSTRACT

Hazardous wastes can be rendered innocuous through chemical (waste stabilization) or physical (waste encapsulation) methods. A research program has been conducted at D. Comrie Consulting Ltd. in order to evaluate geopolymer as an agent for both waste stabilization and encapsulation.

Physical properties of solidified waste and sand mortar mixes have been examined on the basis of compressive strength testing. Abilities of geopolymer to render waste chemically innocuous have been assessed on the basis of leachate testing carried out in accordance with Ontario's Ministry of Environment Regulation 309 guidelines.

Preliminary results show this inorganic binder as extremely effective in reducing metal leachability in a wide range of wastes, and that the physical properties of solidified products make it an ideal candidate for waste stabilization or encapsulation.

INTRODUCTION

Waste treatment can be effected through both physical and chemical processes. Waste treatment and stabilization may be carried out either independent of, or in conjunction with physical encapsulation. While chemical treatment may render the waste itself essentially chemically inert and no longer susceptible to releasing toxins in response to leaching, physical encapsulation concentrates on isolating the waste from interaction with surrounding surface and groundwater.

There are many stabilization agents available for the treatment of toxic waste. Testing of these materials has met with varying degrees of success at reducing the leachability of contaminants in the waste. The purpose of this research program was to evaluate the performance of one such stabilization agent - an inorganic binder known as geopolymer.

GEOPOLYMERS

Geopolymers are inorganic binders consisting of two components: a very fine and dry powder, and a syropy, highly alkaline liquid. Liquid and powder portions are combined to produce a mixture of molasses-like consistency which is then reacted with the desired waste or aggregate. Blending of the two binder components can be readily carried out with the aid of conventional cement mixing technology. The resulting waste-binder mixture can be poured into molds (for example, fibre drums such as might be obtained from a concrete products supplier); drier mixes have potential for extrusion.

The geopolymeric reaction occurs as a result of reacting alumino-silicate oxides with alkali (NaOH, KOH) and soluble alkali polysilicates. Resulting from this reaction is the formation of SiO_4 and AlO_4 tetrahedra linked by shared oxygens. A mildly exothermic reaction in the alkali activated mixture is accompanied by hardening and polycondensation.

The basis of the sialate (or, silicon-oxo-aluminate) network of SiO_4 and AlO_4 tetrahedra is illustrated in Figure 1. Positive ions, such as sodium, potassium, lithium, calcium or barium, must be present in the framework cavities in order to achieve charge balance.

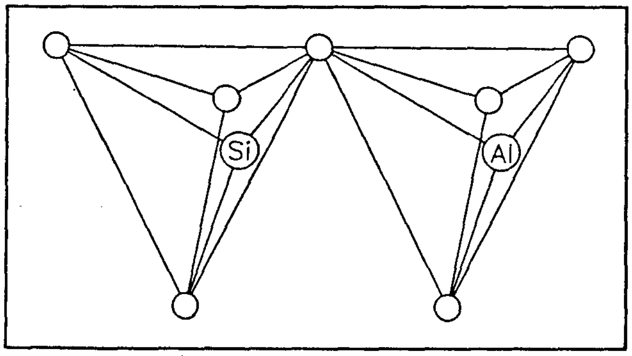

Figure 1: AlO_4 and SiO_4 tetrahedra - basis of the sialate network.

PHYSICAL CHARACTERISTICS

Geopolymers are characterized by a number of interesting physical characteristics, including thermal stability, high surface smoothness, precise moldability and hard surfaces (4-7 on Moh's scale) (Davidovits and Davidovits, 1987). These properties are commonly imparted to products created through a combination of binder with waste materials. In terms of waste stabilization or encapsulation, the most significant physical property imparted by geopolymers is their ability to transform soft, disaggregated or sludge-like wastes into hard, cohesive solids in remarkably short time frames.

Physical testing has been carried out on unconfined cubes created from mortar mixes of sand and geopolymer. Compressive strengths of 40 MPa have been achieved over a 28 day cure period; strengths of 30 MPa (75% of final strength) are acquired in the initial two days of curing (Figure 2). Strengths are acquired with considerable speed in comparison to mortars developed from regular Portland cement (Figure 3).

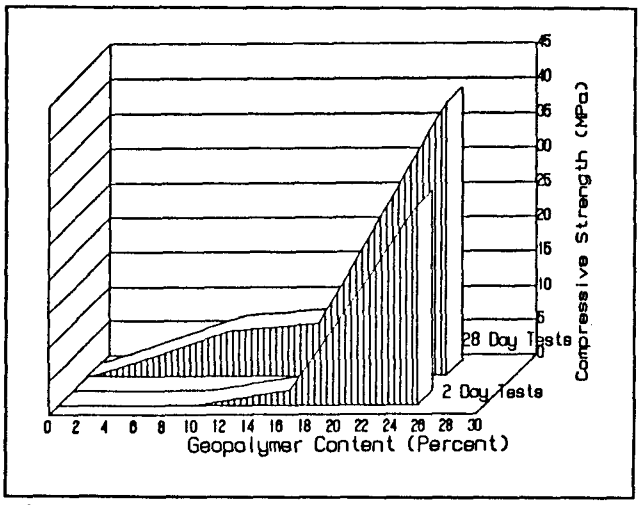

Figure 2: Comparison of 2 and 28 day strengths in inorganic binder based mortars.

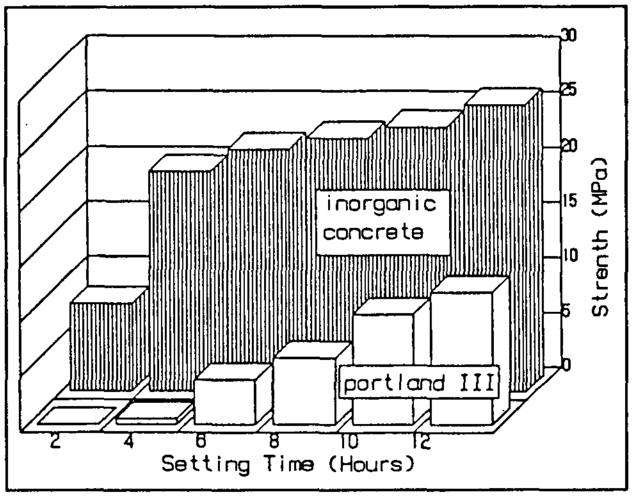

Figure 3: Comparison of Normal Portland and Inorganic Binder Based Concrete Initial Strengths.

In fact, some inorganic binders have been developed to form solid, cohesive masses within one to two minutes of mixing with aggregate or waste forms. Of course, compressive strengths achieved depend on the nature of the aggregate or waste form employed in conjunction with the binder, and the amount of binder used.

CHEMICAL CHARACTERISTICS

In addition to their physical properties, geopolymers are characterized by an ability to resist chemical attack. This is attributed to the fact that, unlike cements, lime does not play a part in the lattice structure which provides the structural strength to the product. The resistance provided against chemical attack is best illustrated by the ability of geopolymer to retain toxins during acidic leaching.

In order to examine this property, a variety of toxic waste samples have been collected from different waste generators. Each sample was split into three and the first portion was assayed for metal concentrations. The second portion was subjected to leachate testing in accordance with Ontario's Ministry of the Environment Regulation 309, Schedule 4 guidelines, calling for pulverization of the sample followed by tumbling in acetic acid. The third portion of each waste was treated with geopolymer and, after curing for 7 days, leach tested. Results were compared with the maximum permissible leachate concentrations allowed by the Ministry of Environment.

Tests conducted on waste at a southern Ontario scrap yard have proved most successful. Bulldozer and soil movement operations at the scrap yard, which has been used for crushing and compacting both automotive and industrial scrap, have resulted in contamination which extends approximately 2 meters down into the soil. Of prime concern is lead contamination, resulting from scrapped car batteries. Analysis of soil from the yard indicates lead concentrations in the order of 6,000 ppm, with 25.3 mg/l leaching out during Regulation 309 style tests. In contrast, samples treated with a geopolymeric inorganic binder leached out only 2.1 mg/l, well below the Ministry of Environment limit for safe emissions of 5 mg/l.

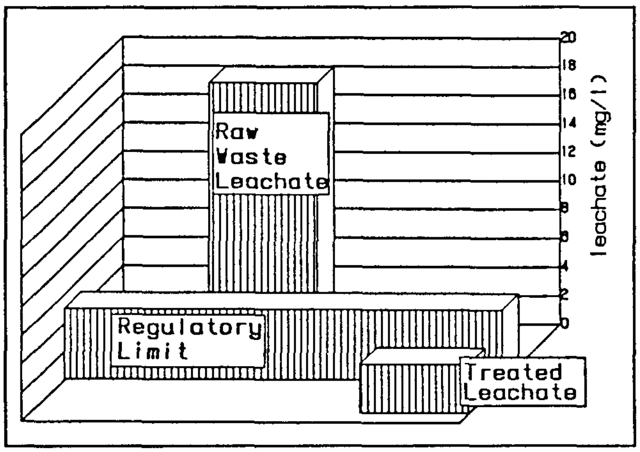

Figure 4: Comparison of Leachate Quality in Treated and Untreated Scrap Yard Waste.

Similar tests were conducted on contaminated soils surrounding a southern Ontario refining and smelting operation. A series of leaks and spills during the plant's forty year operational life have resulted in lead contamination to a depth of three meters. Concentrations of lead in the soil average about 285,000 ppm, with 204 mg/l released to leachate during Regulation 309 style leaching. Geopolymerization brings this level down by an order of magnitude, to 18.3 mg/l.

Figure 5 illustrates the effect on leachate quality as a result of increasing geopolymer content. Ore processing waste (tailings) from an Ontario base metal mining operation was solidified with 10, 15 and 25 weight percent geopolymer.

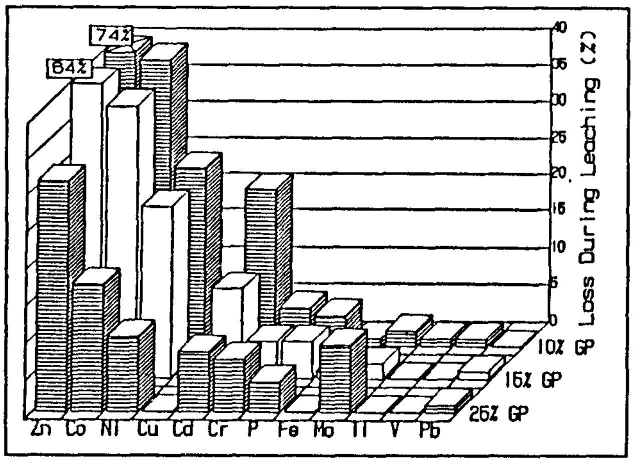

Figure 5: Comparison of % Loss During Leaching - Mine Tailings with 10%, 15% and 15% Binder.

WASTE TREATMENT APPLICATIONS

The physical and chemical properties of geopolymers and of products created with geopolymers makes them attractive candidates for a variety of waste stabilization and encapsulation situations (Comrie, 1988; Comrie and Davidovits, 1988; Davidovits and Comrie, 1988). The automotive scrap yard and the refining and smelting operation noted above represent good examples of possible applications.

Work has already been initiated at the automotive scrap yard on a pilot plant (20 tonne) scale, and contaminated soil has been screened to remove inordinately coarse material which might interfere with the blending equipment. Mixing will be carried out using conventional concrete mixing technology, and the resulting inorganically bound mixture will be poured into fibre barrels. After a short curing time, this solidified and stabilized waste can then be transported to a non-hazardous landfill site, at considerable cost savings over disposal at a hazardous waste facility. This alternative is made possible by the fact that solidification with geopolymer reduces leachate levels to concentrations significantly below those considered hazardous by the Ministry of Environment in Ontario.

Plans for remediation of the refining and smelting site noted above call for a combination of chemical waste stabilization and waste encapsulation. The most contaminated area on the site will be excavated to create an empty "vault", with the removed soil stored nearby. While the vault is lined with low permeability, high strength geopolymer concrete, the soil set aside will be treated with geopolymer to create a solid of minimal leachate hazard. The treated soil will then be returned to the vault and capped with 100 mm of geopolymer concrete, on top of which will be placed an additional 600 mm of top soil. The entire perimeter of the vault will be surrounded with peripheral surface water ditches, resulting in a waste management unit which contains a waste of minimal reactivity and which is isolated from interaction

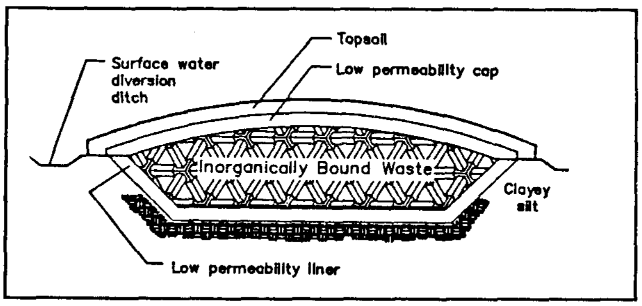

Figure 6: Cross-section of Waste Management Unit for Treatment of Smelter Yard Waste.

with ground and surface water (Figure 6).

The unique properties of geopolymer and inorganic binders, including rapid achievement of high strengths and the ability to immobilize chemical toxins even under conditions of acidic leaching, should result in some interesting future applications.

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INVESTIGATION OF STABILIZING ARSENIC-BEARING SOILS AND WASTES USING CEMENT CASTING AND CLAY PELLETIZING/SINTERING TECHNOLOGIES

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ABSTRACT

Cement casting and clay pelletizing and sintering are two treatment techniques for hazardous wastes containing toxic metals. Research in the past has indicated these techniques may be effective in stabilizing arsenic wastes. Treatability studies using these techniques were conducted on arsenic-bearing soils and wastes present at the Whitmoyer Laboratories Superfund Site.

Treatability study results are presented. The experimental results revealed that cement casting was somewhat effective in stabilizing a calcium-arsenic sludge. Stabilization was enhanced by incorporation of a pre-roasting step prior to hydration or by thiourea addition.

Cement casting was not effective in fixing the arsenic in an iron-arsenic sludge and a sludge/soil mixture. However, pre-roasting the cement-waste combination prior to hydration was effective in promoting waste stabilization.

Clay pelletizing and sintering was partially successful in stabilizing the calcium-arsenic sludge. This technology was not effective on the iron-arsenic wastes, however. In all cases, significant quantities of arsenic volatilized during treatment.

INTRODUCTION

The Whitmoyer Laboratories Superfund Site is located in Jackson Township, Lebanon County, Pennsylvania. Veterinary pharmaceutical products, including organic arsenicals, were manufactured at the site. Prior to 1964, the site operators treated arsenic-bearing wastewater by adding lime to effect arsenic precipitation in an unlined lagoon. When environmental consequences from this practice were noted, the sludge was excavated and placed into a concrete vault, where it currently resides (2). An estimated 2,000 tons of sludge ("vault sludge") containing 370 tons (740,000 pounds) of arsenic were placed into the vault. Other site wastes, including organic chemicals, were also placed in the vault. These other wastes have partially mixed with the sludge. There are concerns about the vault's structural integrity.

The site operator conducted a groundwater pump-and-treat program at