Recent Progresses in Concretes for Nuclear Waste and Uranium Waste Containment

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INTRODUCTION

Radioactive wastes can result from four types of activity:

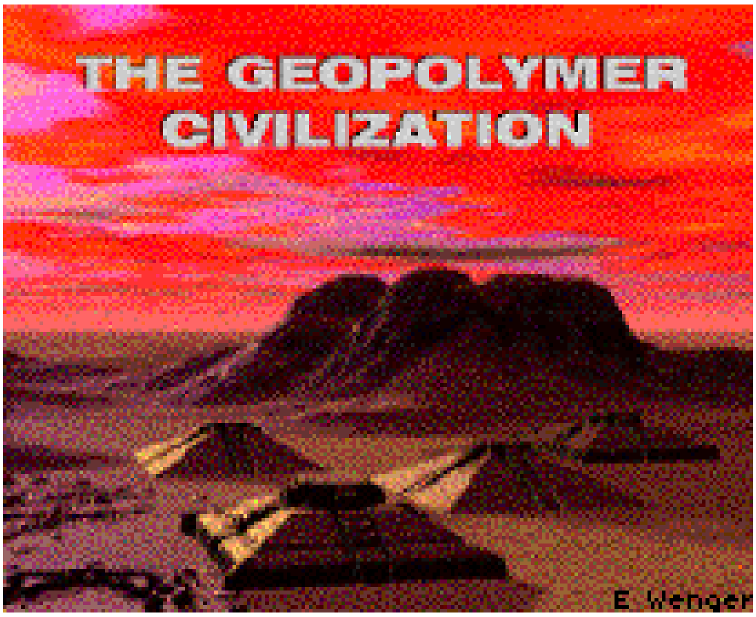
- nuclear electricity generation and the decommissioning of obsolete plants;
- military activities;
- uses of radiation and radioactive materials in medicine, agriculture, industry and research;
- processing of materials that are naturally radioactive, such as uranium ores.

Nuclear and uranium wastes must be managed and disposed of in ways that ensure the protection of people and the environment, now and in the future. The fundamental objective of radioactive waste containment is the protection of people from unacceptable exposures to radiation. This can be achieved by the use of one or more containment barriers to surround and isolate the wastes. The barriers fulfil two roles: they shield people from the radiation emitted by the wastes, and they prevent or retard their movement, ensuring that they do not reach people in unacceptable concentrations. Radioactive wastes can, in principle, be stored indefinitely, given continuing surveillance and maintenance of the storage facilities, including periodic rebuilding when needed.

However, a fundamental principle of waste management is the avoidance of any undue burden on future generations. There is a broad international consensus that the best way of achieving this objective is to dispose of wastes, using a combination of man-made (concrete) and natural barriers, in a way that requires no further action to ensure safety.

Concrete Sentry

The year is 4085. On a broad, sage-studded plain in what had been the western United States of America, 256 monoliths stake out a 32 square-mile rectangle. Inside are dozens of artificial hills, each ringed by more towering monuments. Pictographs and Old Era writings etched into these huge stone slabs warn of danger and demand that people not dig into the mounds. The monoliths and their messages date from the time, two millennia ago, when human were still obtaining energy from splitting atoms and developing weapons by processing plutonium. Local resi-



dents shun the area, believing it to be cursed, but outsiders consider the enormous memorial one the wonders of the Old Era; hovercrafts bring eager tourists daily. The monuments' builders wished these stones to "speak" for at least another 8,000 years, while the lethal and mutagenic substances they warn of slowly exhaust themselves. (Excerpt from an article written in Omni Magazine, by Carole Douglis, titled Stone Sentry, 1983).

Once the waste is entombed for eternity, how do we warn future generations of its potential danger? Signs rust, documents crumble, buildings fail, languages change, places are forgotten. Life and climate 10,000 years into the future may be radically different from what we know today. The issue of Global Warming and its connection with the concrete industry, discussed in another paper [1], shows how fast changes could occur within a time frame as short as two centuries. How do we communicate with humans who may have little concept of the world of 1993 and its symbols? Yet there remains one danger that even the most careful technology and planning cannot eradicate: the possibility that our own descendants may unwittingly release the lethal contents into the environment. Some experts consider the possibility of "human interference" the most significant hitch in long-term geological disposal plans.

It is a question of trying to analyse ancient monuments and incorporate the features that work into a contemporary marking system. Each teaches lessons about monuments that were meant to defy time. Ancient Roman famous concrete structures, such as the Pantheon and the Coliseum in Rome, for instance, have lasted 2,000 years because the material they were built from,*Opus Caementicium* and *Opus Signinum* or Roman concrete, was impossible to dismantled and to be carted away. Other Roman monuments and temples built with regular stone blocks have been destroyed; the state of these monuments also demonstrate that regular hewn stone blocks cannot be trusted as markers, because they tend to be "recycled" for other uses. Acid rain has severely damaged the remains of relatively soft limestone monuments built during the Renaissance (15 Century AD), a fact that demonstrates that these materials cannot tolerate 10,000 years of air pollution.

The markers, fashioned of one piece for durability, would be cast with some of the toughest wind- and water-resistant concretes known. The concrete structures would also be impractical for a would-be recycler to built with. Warnings and danger symbols would be inscribed on them.

THE DIFFERENT LEVELS OF RADIOACTIVE WASTES.

There are many different radioactive elements, emitting several types of radiation, and therefore many types of radioactive wastes, all of which have to be managed in ways that ensure the necessary levels of safety. The different type of waste can, however, be classified into a small number of categories, depending essentially on the concentrations of radioactive material that they contain and the times for which they remain radioactive, with all the wastes in any particular category being managed in the same general way.

The classifications «low», «medium» and «high» relate to the concentration of the radioactivity in nuclear waste and hence to the intensity of the emitted radiation. In time, high level waste becomes medium level and then low level waste; eventually, as with all radioactive materials, the radioactivity decays to nothing.

A separate classification is used for the wastes from uranium mining and milling, and uranium processing. Uranium mining tailings can arise in large volumes and generally contain very low concentrations of naturally occurring radioactive materials, some of which are long lived. Uranium processing involves chemical concentration processes, usually with sulfuric acid, which produce highly contaminated mixed-wastes (chemical wastes, heavy metals and radioactive elements).

There is an important distinction between radioactive wastes, which eventually become harmless, albeit in some cases after a very long time, and chemically toxic wastes, some types of which remain toxic for ever.

NUCLEAR WASTES

1) High-level nuclear waste.

It comes from spent fuel used to power reactors in commercial power plants. High-level wastes remain deadly for up to 10,000 years, the half-life of radio nuclides, or atoms that can be measured in the number of years they remain radioactive. Other high-level waste results primarily from the production of defence materials. The intensity of the radiation it emits is so high that the waste becomes physically hot and remains so for many decades, till much of the radioactivity decays away. It needs cooling, heavy shielding and remote handling devices. It is initially in liquid form and is subsequently vitrified, that is incorporated in hard, stable blocks of glass.

2) Medium level waste.

It comes from nuclear power stations and reprocessing plants (where used nuclear fuel is chemically treated to remove the waste from the reusable fuel) and from medical, industrial and research uses of radioactive isotopes, for example for sterilisation of medical equipment and for cancer therapy. Typically it consists of metal scrap, sludges, resins, and used radioisotope sources. Conditioning generally consists of incorporating the medium level wastes in matrices which solidify into blocks, usually within external containers.

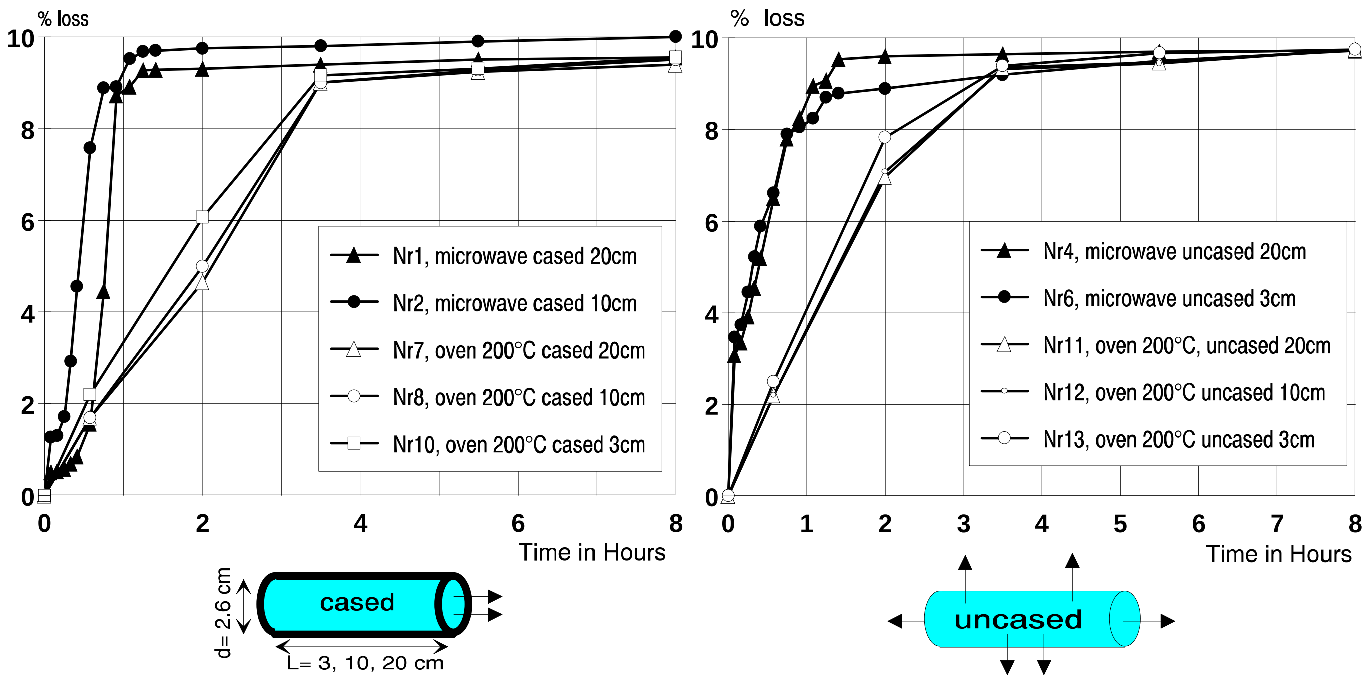
Presently these types of wastes are stabilized with conventional hydraulic cements and the resulting concrete slurry is cast in drums for disposal. One of the main disadvantages of this method is that conventional cements do contain a high amount of bounded water, and the possibility exists of strong radiolytic degradation of this water into hydrogen gas. They do not possess the property required for safe underground disposal, namely the absence of any steam explosion and hydrogen release, resulting from radiations and heat generated by the confined radioactive waste. Dewatering of Portland cement based radioactive waste forms is a slow and difficult process which often leads to consequent cracking of the waste-form.

Concretes made of Geopolymer cements provides two advantages:

1) the structure enables fast dewatering and the material remains stable at temperatures up to 1000°C.

2) the radioactive elements are trapped within the zeolitic geopolymeric framework, enhancing the innocuity of the containment.

A study performed by the German Battelle Institute, Francfort [2, 3], was carried out in order to demonstrate the potential provided by superfast microwave drying of Geopolymer based radioactive waste-forms. Each sample consisted of commercial K-PSS type Geopolymer binder TROLIT®, cast in glass cylinders, with various lengths: 20, 10 and 3 cm. After curing at 85°C for 0.5 hours, 6 samples were demolded, and 7 samples remained in the glass cylinders. In the Fig.1, these samples are named «uncased» and «cased», respectively.



The main advantages of microwave drying are:

1) The water content can be reduced to values below 1% within very short time.

2) The efficiency of microwave drying is practically independent from the shape of the waste-form; identical results for 20cm, 10cm and 3cm long samples.

3) The efficiency of microwave drying is practically independent from the exposed surface; identical results for «uncased» and «cased» samples

Figure 1: Microwave drying, 300W power, vs. oven drying at 200°C, for cased and uncased Geopolymer waste-forms; the sample area where evaporation takes place is visualized by arrows; Potassium-Poly(sialate-siloxo), K-PSS, type TROLIT® binder. Oven drying is fast and do not generate any stresses but microwave drying is superfast.

In terms of safe containment, Geopolymeric concretes allow the ultra rapid microwave processing and drying of radwastes and do represent a valuable alternative technology for the disposal of medium-level nuclear wastes. Geopolymeric materials do possess the property required for the underground disposal, namely the absence of any hydrogen release and steam explosion, which result from the action of radiations and heat on water.

3) Low-level waste.

Much of this waste holds only small amounts of radiation that break down quickly. Since it emits so little radiation it needs no special shielding and is handled using simple protection measures such as rubber gloves. It comes from nuclear power stations and other nuclear installations and from research centers, hospitals and radioactive materials. Typically it consists of paper towels, used syringes, clothing, gloves, glass, cleaning material and anything that comes in contact with radioactivity is considered low-level waste. These types of wastes are stabilized with conventional hydraulic cements and the resulting concrete slurry is cast in drums for disposal.

Of similar radioactivity are many wastes from the nuclear industry, particularly the large quantities of scrap that result from the dismantling of obsolete installations and also the large amount of liquid low-level radioactive defence tank wastes. A paper by H.L. Benny [4] outlines some interesting information on the campaign aimed at providing a permanent disposal for the low-level portion of Hanford Site defence tank wastes. The Hanford Site, Washington, was selected in 1943 to produce nuclear materials, mainly plutonium, for the production of nuclear weapons. There will be approximately 44 disposal campaigns of about one million gallons of waste each, solidified with 900.000 pounds of a dry blend (1078 kg/m^3) consisting of 47% blast furnace slag , 47% fly ash and 6% Portland cement, with up to four campaigns per year. Generally, the waste contains 12% by weight of strong alkali NaOH and hardening of the cementitious material in the grout results through alkali-activation, a technique first developed by Glukovsky [5] for blast furnace slag, then enhanced by the author in advanced geopolymeric cementitious materials [6].

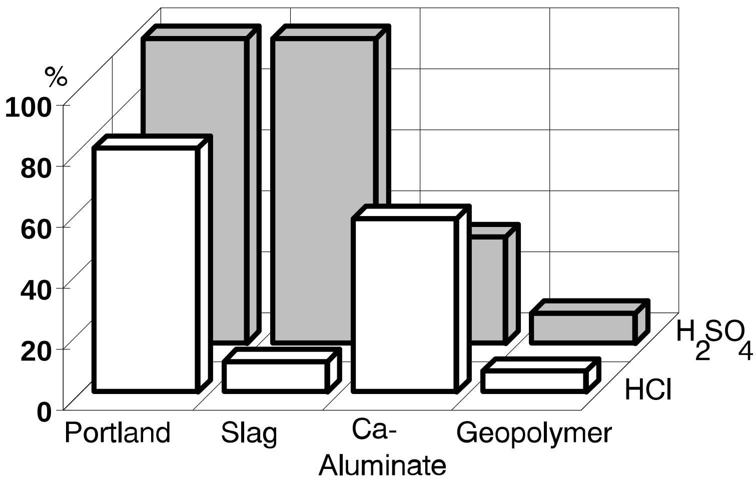
URANIUM WASTES

Uranium mining and milling waste

To extract uranium, typically huge amount of gangue minerals must be mined with the ore. The gangue is usually separated from the ore at a mill close to the mine site and is disposed locally. These mine tailings are subject to weathering and ground water seepage, leaking into surrounding environment. Tailings from uranium mines contain heavy metals (vanadium, lead, barium, bismuth, arsenic and others) and radium. They also have often high sulfide contents. Weathering and subsequent oxidation produce sulfuric acid, which seeps into the environment, leaching and carrying the toxic heavy metals and radium with it. 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 (300 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} to 10^{-3}
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 leachates. 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 been previously described [7]. They have three goals.

The first goal is to seal the hazardous materials into an impermeable monolith. This prevent the direct contact of potential leachates, like ground water and percolating rain. Unlike conventional Portland cement, geopolymeric cements do not rely on lime and are not dissolved by acidic solutions (Fig.2). 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.

Figure 2: Break up in acidic environment (5% solution) for Portland cement, blended slag/Portland, Ca-aluminate cement and Geopolymer.

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. Geopolymeric binders and cements are the synthetic

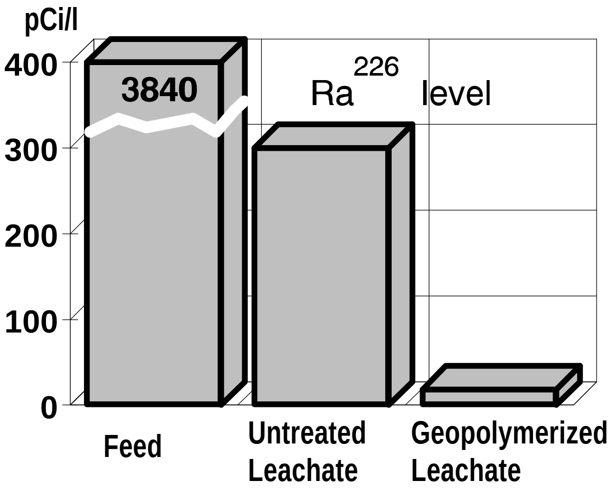


Figure 3: Radium level in uranium waste tailing (acid leaching, constant pH 5, Reg. 309), Potassium-Poly(sialate-siloxo) K-PSS type GEOPOLYMITE® binder.

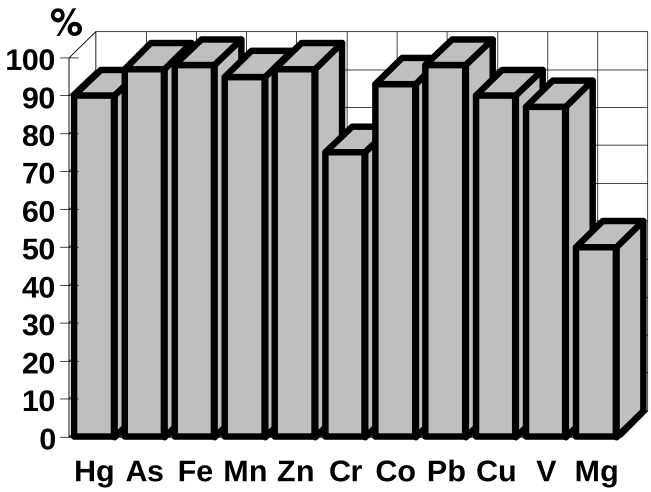


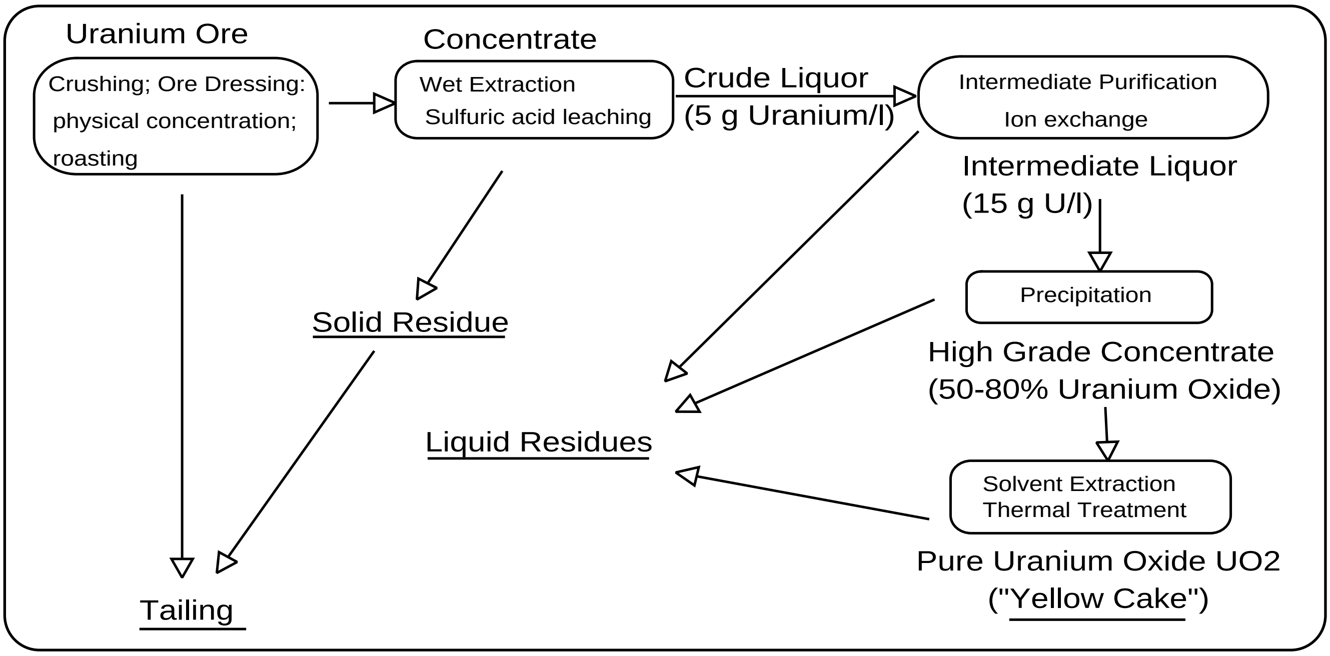
Figure 4: Efficiency of geopolymeric cements, % of trapped heavy metal (acid leaching, constant pH 5, Reg. 309), Potassium-Poly(sialate-siloxo) K-PSS type

analogues of natural zeolitic materials (zeolites, zeolitic tuffs, pozzolans) which are known to contain safely heavy metals and radioactive elements. A Canadian research program on toxic waste stabilisation was funded by CANMET Canada (1988) (Canada Centre for Mineral and Energy Technology) [8]. Fig.3 and Fig.4 display examples of the results obtained at Ontario Research Foundation (Canada) on the innocuous solidification and stabilisation 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.

The third goal is to make a durable monolith that weathers environmental stresses. Using ancient building materials from Rome and earlier civilisations as models, we are able to formulate durable, impermeable monoliths which will endure at least 2,500 to 5,000 years of weathering. 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.

Uranium Processing waste:



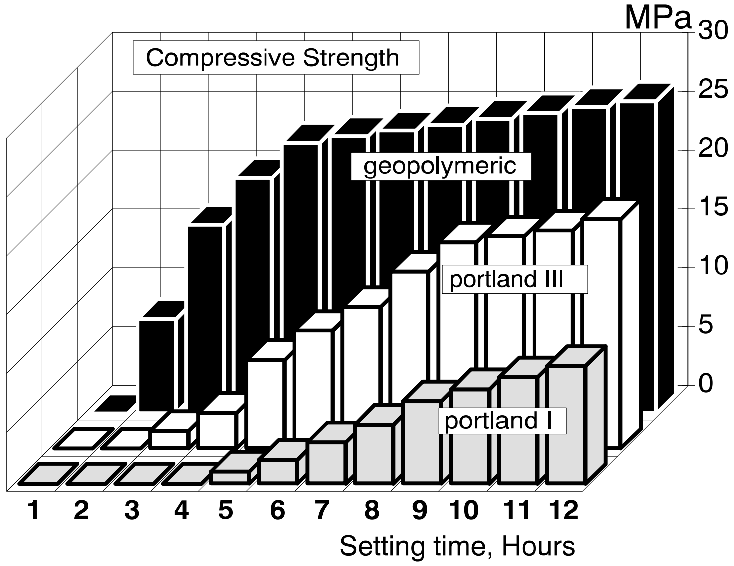
The opening to the western world of Eastern Europe and the former Soviet Union has brought to light the severe contamination and pollution of numerous industrial sites. Those dealing with the extraction and processing of uranium ore represent the heaviest pollution ever encountered so far.

The author is the principal coordinator of a major European research program, called GEOCISTEM, aimed at manufacturing cost-effectively new acid-resistant geopolymeric cements specially designed for the rehabilitation of these severely contaminated sites, in particular the former Soviet-East German site located in Saxony (south-west of Dresden), Germany. From 1950 to 1990, the Soviet-East German company Wismut, was the third biggest world producer of concentrated uranium oxide, the «yellow cake», after USA and Canada.

Uranium ore normally contains only a few hundred ppm (part per million) uranium. The ore is processed and concentrated in order to get pure uranium oxide UO2 (yellow cake), resulting in the accumulation of a wide variety of radioactive and chemical waste. A typical flow sheet is shown in Fig. 5.

Figure 5: Extraction of uranium oxide from the ore

The first extraction step involves a chemical dissolution of uranium oxide with concentrated acid, sulfuric acid or nitric acid. The acid solid residue, dumped in the areas surrounding the milling and processing sites, contains radium and heavy metals such as vanadium, lead, barium, bismuth, arsenic and others. The various solutions used during the different concentration steps, either acidic or basic, still rich in heavy metals and radioactive elements, were pumped into large decantation ponds which have leaked and contaminated the surrounding soils. At the German site of Wismut, at least 52 square kilometers (10,000 acres) are severely contaminated and 200 square kilometers (50,000 acres) less contaminated.



According to the German Ministry for Industry and Mining, 16 billion DM (10 billion dollars) will be needed, during the next 15-20 years, only for the clean up and rehabilitation of this site. The GEOCISTEM program will determine the basic properties of concretes elaborated with the new acid-resistant geopolymeric cements. Emphasis will be put on the uses of local polluted aggregates and durability of the manufactured concretes. Designed materials and technology will be applied to borehole plugging, shaft sealing, geological barriers for underground containment, cappings, dam and walls, insitu immobilization for above-grade impoundment and radon suppression capping..

The properties of Geopolymer binders include high early strength, low shrinkage, freeze-thaw resistance, sulfate resistance and corrosion resistance; they are good for long-term containment of toxic and hazardous wastes. The rapid hardening geopolymeric cement develops compressive strengths higher than 15-20 MPa as early as after 4hours at 20°C (Fig.6). The final 28-day compression strength is in the range of 70-100 MPa.

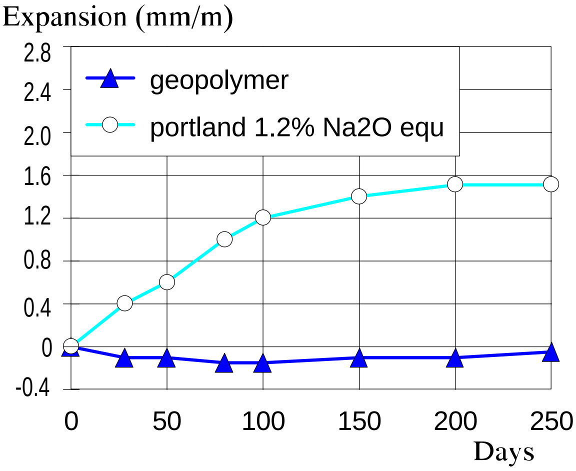


Figure 7: Alkali-Aggregate Reaction; ASTM C227 bar expansion test on PZ-GEOPOLY® Geopolymer cement and ordinary Portland Cement.

Table 2: Oxides and Alkali content, % by weight, in Geopolymeric cement and natural pozzolans.

	PZ-GEOPOLY®	Pozzolan	Rhineland Trass
SiO_2	59.16	54	57
Al_2O_3	17.58	19	20
CaO	11.1	10	6
MgO	2.93	1.5	2
K_2O,Na_2O	9.2	10.6	7

Figure 6: Room temperature setting for concretes made of geopolymeric cements (PZ-GEOPOLY®) and Portland cements.

Long-term durability of concretes made with local aggregates, for barriers and walls.

The fostering of alkali-based geopolymeric cements will mean a dramatic change in the normative development presently carried out on Portland cement related concretes. Alkalies are generally thought of as the cause of deleterious Alkali-Aggregate-Reaction. As a consequence, the tendency has been to avoid any addition of alkali in ordinary Portland cement and commonly to require from the cement manufacturers the supply of low-alkali cements. Preliminary studies involving 27Al MASNMR and 29Si MASNMR nuclear magnetic resonance spectroscopy [9], shows that geopolymeric cements are the synthetic analogues of natural pozzolans which are known to effectively suppress the alkali-aggregate reaction. The chemical make up of geopolymer cement is close to that of Italian pozzolan and Rhineland trass (see Table 2). Fig.7 displays the results of the tests carried out according to ASTM C227 bar expansion.

Geopolymer cements, even with alkali contents as high as 9.2%, do not generate any dangerous alkali-aggregate reaction.

CONCLUSION

We mentioned above that, because alkalies are generally thought of as the cause of alkali-aggregate-reaction, the present tendency is to avoid any addition of alkali in ordinary Portland cement. According to the terminology generally in use by cement scientists and concrete experts, geopolymeric cements should be named «alkali-activated cements» [10]. The concept of Geopolymer and Geopolymerization is well accepted in the science and technologies involving advanced materials. Geopolymers result from the polycondensation of polymeric alumino-silicates and alkali-silicates, yielding three-dimensional polymeric frameworks. Cement scientists should admit that cements having alkali contents of 9.2% and higher, which do not generate any dangerous alkali-aggregate reaction, cannot comply with the existing codes and guidelines and should get a distinct appellation. It becomes obvious that the terminology in use generates confusion and is a severe obstacle for any further beneficial scientific and technological developments of alkali cementitious systems. To call them, for example, Geopolymer cements or Geopolymeric cementitious compounds, focuses on their unique properties without being confused with regular alkali-activated Portland cements.

The main objective in the management of nuclear and uranium radioactive wastes is to protect current and future generations from unacceptable exposures to radiation from man-made materials. This task can best be achieved by the use of one or more containment barriers to surround and isolate the wastes. The barriers fulfil two roles: they shield people from the radiation emitted by wastes, and they prevent or retard their movement, ensuring that they do not reach people in unacceptable concentrations. The main requirement is then to ensure that wastes remain isolated from people for the necessary length of time. This will vary, depending on the type of waste. There is an important distinction between nuclear wastes (high-level, medium-level and low-level), which eventually become harmless, albeit in some cases after a very long time, and uranium wastes which comprises radioactive wastes and chemically toxic wastes, and therefore will retain their toxicity for ever. The engineered structures of the repository are designed to stay intact for several centuries. After several thousands years, ground water will gradually penetrate the repositories and cause corrosion of the concrete structures. At this time, the radioactivity of the wastes will have fallen to a small fraction of its initial value, but chemical waste will remain toxic and harmful for the environment.

Geopolymite and PZ-Geopoly are registered trademarks of Géopolymère & Co; Trolit is a registered trademark of Hüls AG.

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