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From Ancient CONCRETE TO GEOPOLYMERS

The act of creating a business cannot be reduced to the offer of competence and given products at an appropriate time. It often implies particular kinds of people, because the path, filled with obstacles, always makes the course difficult. Even though these people may have a certain number of qualities in common, like willpower or a goal-oriented spirit, they differ greatly in their character and in the situations they are faced with.

We were given the opportunity to meet Prof. Joseph Davidovits, and to discover the path that made him start as an organic-polymer chemist and become a mineral-polymer chemist. And this path is not dull.

In 1970, a horrible fire burned down the French nightclub "Cinq/Sept."This was cruel proof that polyester-type decoration materials represent an unthinkable danger. At the time, Joseph Davidovits was in charge of a textile research laboratory in Saint Quentin, France. In his field, he was on several occasions confronted with the danger of flammable nylon stockings and overalls, which caused several severe accidents in the workplace.

Given the situation, it was absolutely necessary to bring non-flammable materials to the market. Everyone in the chemical industry knew that this was possible by introducing phosphides into the chain. However, phosphides are toxic products that one cannot conceive of using, for it would be substituting one evil for another. In fires, the greatest danger is not the flame, but rather the release of toxic smoke. Joseph Davidovits decided to actively address this problem and start his own business in 1972.

Learned Language is mandatory

The whole problem was to create non-flammable plastic materials, not based on carbon chemistry. The solution was to use silicon based geological elements. But one had to overcome the difficulty of getting the operation to work at low temperature.

"Thus", explains Joseph Davidovits, "we discovered that some mineral chemistry reactions are similar to some used in organic chemistry." This observation led to the first applications based on the transformation of clay at low temperature. An interesting application was the manufacture of non-flammable wood-chip panels. Their utilization could undoubtedly have prevented, in the early seventies, the disastrous Edouard Pailleron high school fire, in Paris. The corporation Saint Gobain was very interested in the product, and programmed a complete prototype manufacturing line. There was an important market. But the 1973 oil crisis disrupted further progress.

◆Getting rid of the art of firing

The first objective of Pr. Joseph Davidovits' research on "geopolymer" materials was to create an alternative to polymers with regard to ease of use.

The success of plastic materials is primarily due to low temperature setting. Plastics do not require a firing procedure, and unlike to ceramics and metals, temperatures under 100°C are sufficient.

By substituting mineral elements, such as sodium or potassium silico-aluminates, for organics, the manufacturing process of geopolymer becomes that of a mineral polymer. It therefore naturally displays an exceptional fire-resistance quality, which may be put to use in fire protection applications (panels, doors, and the frame of airplane flight recorders). Although the geopolymeric manufacturing process eliminates firing, fire may present an indispensable need for its utilization!

◆Future applications

Geopolymers are at the dawn of their use, especially in the area of high-technology. So far, geopolymeric molds exist to form titanium alloy for aeronautical components and ladles that endure permanent contact with molten aluminum. But these have not been widely industrialized.

The main problem for this type of new product is designers' habits. We are all familiar with the way spheroidal graphite cast iron was brought

▲Silico-aluminate: synonymous of polysialate.

▲Polysialate: large molecular chain made of silicon, oxygen, and aluminum. It is one of the main constituents of GEOPOLYMER.

▲Mineral polymer: a polymer is a very long chain of atoms which repeats itself. A mineral polymer is primarily made of silicium, oxygen and aluminum.

▲Organic polymer: long chain made of carbon, nitrogen, oxygen and hydrogen atoms. It is also called carbon chain, and is the prime constituent of all living beings, crude oil, and plastics.

▲Geopolymer matrix composites: composite materials are made of fiber glass, carbon, or graphite fabric; the binder which is used to harden this fabric is called a matrix.
Here, the matrix of the composite is the Geopolymer binder.

▲Thermoplastics: materials which become soft through heat (iron, steel at 800°C, PVC at 180°C, Nylon at 250°C, etc...) and behave their shape upon cooling.

The crisis stalled development of the product to the point at which Joseph Davidovits was forced to lay off his employees, and he found himself alone. The business had to be re-thought by analysing any mistakes. The system had to be changed, and the business had to be oriented towards high-end applications. In high-tech applications, geopolymers have a role to play. The mineral resins are silico-aluminates. They withstand temperatures of 1000°C to 2000°C. With this established, specific outlets had to be found for the products. "In my mind," notes Joseph Davidovits, "I thought to show the technological community the importance of developing a new branch of mineral chemistry. But oddly enough, the potential applications did not attract attention. They were thought to be only the return to the processing of clay, which was considered trivial even though an intelligent retransformation."

A wall of misunderstanding had been instantly erected. The influence of high technology is such that it rejects anything that could be acquainted with a de-volution process. Within such a mind set, clay was no longer interesting. The idea of recreating clay was not considered a noble course of action. Under such circumstances, the promotion of clay technology did not seem credible. Thus, our interviewee sourly realized that Moliere's learned people would continue to rage and that one had to serve them with the language they desired. " This is why I eradicated from my vocabulary the term clay," says Joseph Davidovits. "I talked instead about polysialates. And I did lectures." The first of these public appearances took place in Stockholm, in 1976. My topic was "the heat stability of mineral polymers (as opposed to organic polymers)." But it was in 1979, in Los Angeles, that a real reference to geopolymers was made. Into the field of reinforced textiles, Joseph Davidovits introduced the novel idea of a geopolymeric matrix by showing the thermal stability of textile fibers. As interesting as this may be, his research was at the time far from complete. It was not yet possible to create geopolymer-matrix composites. Nevertheless, -and this may illustrate why the innovator must promote his findings- the property of thermal stability attracted attention. The Dassault corporation, in particular, showed interest in the idea. This company consequently oriented the research of Joseph Davidovits' team towards the aeronautics field.

In the beginning (1980), the property of thermal stability was used in the transformation of thermoplastics. The scope was then widened to the casting of super-plas-

into use, by an accidental fall from a great height of tubes made out of this type of cast iron. Against all expectations, theses tube were bent without breaking, as if they were made out of steel. The traditional idea that cast iron was brittle was eradicated and permitted the fabulous development opportunities that ensured for security elements made of spheroidal graphite cast iron.

◆The mortars

Mortars are made of lime or cement, which act as binders for the so-called fillers. Lime is made by calcining limestone (calcium carbonate $CaCO_3$ dividing in lime CaO and carbon dioxide CO_2). Regular lime is hardened through the action of carbon dioxide contained in the atmosphere; a mortar containing this lime will not withstand erosion because its mechanical properties are mediocre.

If the limestone contains a portion of silico-aluminates, or if clay is added to it, the product will harden, after calcination, without the presence of air, for instance under water. In that case, lime is called "hydraulic," and its mechanical properties have been improved.

If the portion of silico-aluminate added is significant, along with other elements, such as aluminum, iron, magnesium oxides, and so on, then a cement is obtained. Mechanical properties will vary according to the proportion and nature of each element included.

Roman mortar (Trier, Germany). Made of white lime and red powdered brick (testa in Latin) .The «testa» contains the elements necessary to start the geopolymeric reaction and the hardening of the mortar.

▲Crystallization: sugar is made of crystalline powder, whereas caramel has an homogenuous amorphous structure and is more difficult to break apart than regular sugar. When a polymer crystallizes it becomes generally weaker.

tic aluminum, which is processed in a 500°C to 550 °C temperature range.

Presently, the trials deal with titanium alloy tools operating between 900°C and 950 °C. So far, the results seem promising. To date, these geopolymeric products, geared towards the aeronautics industry, are technically and economically competitive. Their share of the European market has recently started to increase. But Joseph Davidovits notes that it has taken them 10 years to specifically meet the needs of this industry.

"One thing is certain," he says, "we were at the time technologically far ahead. But we weren't given the opportunity to benefit from it." He points out that French products are often faced with a lack of credibility in their own country, whereas American products are blindly granted credibility. In order to foster the superiority of his product, the French industrialist has to make considerable amounts of risky investments and undertake considerable financial efforts to gain operational stage. This was done without any immediate commercial compensation, to the risk of jeopardizing the whole enterprise. The problem is even more complicated when everything dealing with high-technology (and not only in this field) seems to be built on the American market, which is very hard to penetrate. In fact, notes our interviewee, the promotion of a European product begins on American soil. "That's exactly what happened with our material." Everything really started in Los Angeles, in 1990, with a presentation, followed by another one at a symposium in San Diego. It is a sad fact, but from now on the U.S. seems to be a mandatory route to success.

The American based presentations keep French and European engineers informed on trends, evolution, and new products. Each year, a certain amount of time is dedicated to conferences and meetings, which are often held in Florida and California. It is also, indirectly and in a subtle manner, how America watches the developments of European technology.

Being able to measure one's Lead

Entrepreneurs, having a high-value-added material available, and a seemingly promising future, cannot wait for success to knock on their doors. They must seek their battle grounds, especially when dealing with a new product like geopolymers that is aimed specifically towards the aeronautics industry. Joseph Davidovits explains that the different potential applications for mineral polymers had to be carefully studied. Let us recall that the

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Pozzolans are volcanic minerals, mainly made up of aluminum, iron and silicon oxides. These naturally possess hydraulic properties. This explains the durability of Roman monuments built with mortars containing pozzolans from the Vesuvius volcano! These properties can be re-created by calcining clay or using fly ashes collected at electricity coal power plants.

◆**If...**

Let us suppose that the abbey of Cluny (France) was built out of rubble stones (concrete) or mortar-bonded bricks rather than carved limestones. This monument would certainly not have been demolished after the French Revolution in 1789 due to the low value of these materials.

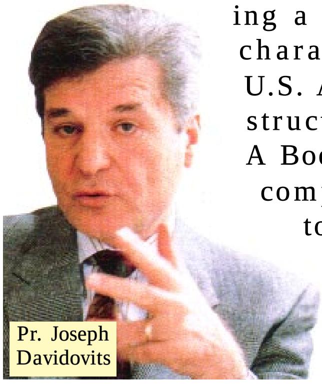
Since the decline of Ancient Greece, it is apparent that every construction, marble pillar or squared-off stone is a potential quarry! But in order to build edifices with rubble stones, more erosion resistant binders than regular lime must be available.

The high-quality mortars used by the Romans more than two thousand years before, were unknown in Burgundy at that time. However, the Saint Sofia Church of Constantinople was built in the year AD 532 using the Roman concrete technology. The same applies to the cathedral of Irevas. It is by trying to match the properties of binders used in the famous buildings of ancient Rome that Aspdin invented Portland cement. He was calcining clays from the Leeds area. Meanwhile, the French Vicat was doing the same to clays from the area of Grenoble. This took place less than half a century after the demolition of Cluny III!

▲Calcining calcium carbonate: means the burning of limestone, yielding lime. Adding water to lime, results in a binder which has been the basic formulation of all mortars since 10,000 years

difference with organic polymers (PVC, polyacrilates) lies in the absence of a carbon chain. One can, in that case, at an industrial level, resort to the chemistry of polymerisation, using sodium or potassium silicoaluminates. The operation of crystalization is thus avoided. And from that point, it is possible to obtain not only a resin but also a binder and a cement.

Cements were precisely the option chosen by Joseph Davidovits . As with all innovators, he had to innovate. Research was oriented along two main lines: new kinds of cement, and hazardous and radioactive waste management. Joseph Davidovits and his team have been developing a new kind of cement with exceptional characteristics. This cement, used by the U.S. Air Force and others, enables the construction of a runway in a very short time. A Boeing can land on it only 4 hours after completion. These properties are believed to be useful for other fields, such as hazardous and radioactive waste management. Joseph Davidovits pointed out that such a cement would be an ideal material for the long-term confinement (trapping) of heavy metals, because it recreates natural rock. And once again the product was too advanced for the needs of its time. "In 1987", Davidovits continues, "only two countries were demonstrated to us an interest, Canada and Sweden. It was therefore not in the U.S., where I was working at the time, that I could begin trials, but in Canada. I had to negotiate very hard to begin these trials, which would prove that my technology could really trap toxic materials such as mercury. I finally found a laboratory in Toronto, and a partner in Ottawa." However, the price outweighed the results of the trials. The material was too expensive, and so this means of stabilization was disregarded. One must add that in 1987, the environment was not a major political issue. The "green" parties were not being courted by those in office. Joseph Davidovits tells us the innovator's greatest challenge. “One must know how to innovate by taking just enough lead to raise interest. To much lead creates a reference vacuum, which is likely to scare the end-user away. Will the product be trustworthy? Will it not modify my behavior as a user? Is it not better to wait for a competing product to appear which will benefit from the flaws of the first one? Moreover, unforeseeable economic and sociological consequences weigh upon these questions (such as the soaring of the "green" parties). With the new geopolymer cements, Davidovits now possesses a material tailored to the market. We keep in mind that the manufacture of traditional Portland cement requires calcining calcium carbonate. This yields calcium oxide and so the emission of carbon dioxide gas. In low quantities, this not considered a major concern. This changes on a global scale. What is happening



Pr. Joseph Davidovits

◆The Souillac Bridge

After his graduation from the Ecole Polytechnique, Louis Vicat, based in Perigueux as a civil engineer, was in charge of a bridge construction project over the river Dordogne, at Souillac.

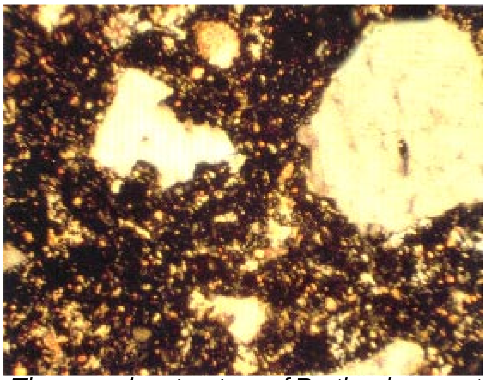
Very little was known concerning mortars in 1811, and Vicat decided to research binders suited for bridge construction. The underwater part of the bridge imperatively required a hydraulic hardening binder. He published his first findings in 1818 under the title "Recherches Expérimentales sur la Chaux de Construction, les Bétons et les Mortiers" (Experimental Research on Construction Lime, Concretes and Mortars). His second paper entitled "Résumé des Connaissances Actuelles sur les Mortiers et les Ciments Calcaires" (Summary of today's knowledge on limestone mortars and cements) was published in 1828. It was to become a standard reference. However, four years earlier, the Englishmen Joseph Aspdin invented Portland cement by calcining a mixture of clay and limestone.

◆The missing link

Regular lime does not withstand the test of time. The majority of the constructions using this binder have long since disappeared. How can it be explained then, that certain edifices are still standing, and that their mortar is as resistant as our best hydraulic binders? It is likely that works built to last were made with specific know-how, whereas eroded buildings lacked it. The durability of this ancient mortar is mainly due to fillers such as alumino-silicates. Regular lime

today is the soaring of worldwide cement and concrete needs, especially in industrializing countries (Asia).

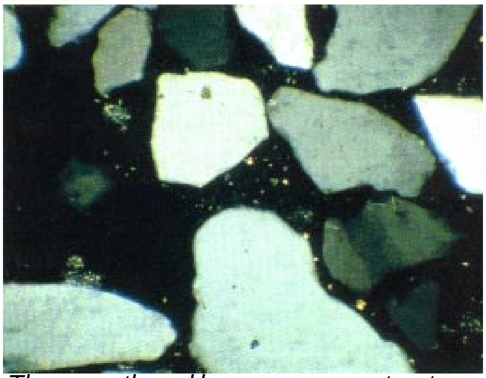
The first stage of all industrialization, increasing standards of living, requires concrete for building infrastructures. The example of China is significant, given that its production started from 40 million tons in 1976 and has presently reached 250 million tons. Countries such as India, South Korea, and to a lesser extent Taiwan and Thailand, are among the worlds largest producers.



The granular structure of Portland cement surrounding sand explains its weakness because the structure is not compact.

The emission of carbon dioxide is, therefore, becoming a growing concern; it is an important contributor to the greenhouse effect. As it regards development statistics, the worldwide level of cement production, estimated at 1.8 billion tons by the year 2000, is expected to reach 3.5 billion tons in 2015. This would put the share in the global pollution (all human activities combined) at 18%. "One can easily understand," explains Joseph Davidovits, "the importance of these new geopolymer based cements, which would lower the cement-related emission of CO_2 by 90%." Such a prospect could greatly increase the feasible production of cement and concrete in the developing countries. The drastic limitations planned by the EEC and the USA would also be eased.

A Disturbing Hypothesis



The smooth and homogenuous structure of Geopolymer cement surrounding sand, yields a stronger cement.

Our interviewee made clear to us that all his reflections on cement derived from questioning the nature of ancient Egyptian and Roman mortars. Their resistance presents a mystery that lay in the materials they contain. What are the ingredients, which, when added to lime, gave these materials such strength? The common interpretation is that it is a lime-based mortar, and all materials are "inert" (without chemical reaction) except for the lime. "Our interpretation," states Davidovits, "is just the opposite. It is that reactive ingredients combine with lime, leaving the excess lime as *inert*." The makeup of the mortars varys according to the archeological site, that is, according to its geological environment. A mortar will be good if components are selected from an appropriate site.

In 1979, at an Egyptology congress, Joseph Davidovits set forth the hypothesis that the pyramid blocks were cast as concrete, instead of carved. Such a theory

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does not have a binding function in this case. This knowledge appears to have been lost after the fall of the Roman Empire, for concrete disappeared from masonry uses and for many centuries. It was only in the 19th century, after the publication of Vicat's works in 1828, that knowledge expanded again, and explained the increase of mechanical properties through hydration reaction. This led the way to fabulous developments such as reinforced and prestressed concrete.

◆ **Roman cement**

Ancient cement such as the Romans made, gives us an idea about the durability of geopolymeric cements. This is important because it is possible to extrapolate the durability to hazardous waste management systems.

◆ **The GEOCISTEM project**

The European Community, under the "Brite-Euram" research funding program, is supporting the European industrial research program named GEOCISTEM.

Its purpose is to develop the technology and equipment necessary for the manufacture of geopolymeric cements on an industrial scale, at a cost close to that of traditional cements. Joseph Davidovits is the coordinator of the project. GEOCISTEM stands for Cost Effective GEOpolymeric Cements for Innocuous Stabilization of Toxic Elements.

was great disruptive to the orthodox theory with its hundreds of thousand of workers taking part in this gigantic endeavor.

But in the course of his research, and after performing chemical analysis on the cement materials, he concluded that ancient Roman cement and the Great Pyramid blocks were the result of a geopolymeric reaction or in other words, a "geosynthesis." And thanks to this historical reference, he was able to demonstrate that Geopolymers have the same strength and endurance than natural rock.

Of course, Joseph Davidovits is innovative. He uses archeology as a data bank, to validate his discoveries. This shows the originality of his scientific and industrial approach.

But his approach has its difficulties, as it requires a critical examination of data that is thousands of years old. Imagine the numbers of natural processes that have had time to act on the ancient mortars. There is a risk of misinterpretation, so one must proceed caustiously. Another source of potential errors arises from ancient scriptures, which have been translated through the centuries in diverse ways. Interpretations devoid of the new information increase confusion, and these are standard references. What is required are new translations employing the new science along with knowledge of antiquity, as well as a formidable creative capacity.

Adapted from «Arts et Métiers magazine», Jacqueline Delatte et Gérard Facy, 09/93.

A street of the Roman city Pompei

GEOPOLYMERE ®

▲ **What is geosynthesis?**

Geosynthesis is the science of manufacturing artificial rock at a temperature below 100°C, in order to obtain natural characteristics (hardness, longevity, heat stability, etc.). The Geopolymer materials and the Geopolymer-based mortars, cements, and binders, are geosynthetic materials. This word was coined to broadly define the geopolymeric chemistry.