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PRE-PORTLAND CEMENTS AND GEOPOLYMERS

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ABSTRACT
This paper presents the historical background of the 20th-century technology of geopolymers in light of a literature research of the 15th to 19th centuries and offers a hypothesis on why this historical knowledge was forgotten when Portland cement appeared. The recapitulation of the different cementitious calcareous matters returns all the way to the Bible builders; Ancient Vitruvius Pollio's work "Ten Books of Architecture". These books were not only read but practically proven in pre-Portland times and especially at the beginning of 19th century. The long-term stability of Roman mortars and constructions was studied from the perspective of the cementitious materials, and the cited literature demonstrates the historical evolution of calcareous cements, then the reasons for the interruption of progress and return to the historical experience in the 1980s.

KEYWORDS: Caementum, Cementitious, Calcareous cement, Hydraulic cement, Roman cement, English cement, Cement of Boulogne pebbles, Pouilly cement, Russian cement, Cement of Baye, Aqua-fortis cement, Plastic cement, Parker's cement, Common cement, Portland cement

A REVIEW ON CEMENTS

The long human history of masonry is directly connected with the possibility of joining stones and bricks with mortars. We usually think of calcareous mortars, which according to the archeological researchers are older than pottery – call these times the pre-pottery time, having its evidence in constructions from the Middle East (Kozlowski and Kempisty, 1990; Rollefton, 1990). The knowledge of lime burning could then be labeled as the first pyro-technology, which changed natural stone by a targeted purpose (Gourdin and Kingery, 1975; Kingery et al., 1988).

The Egyptian mortars from the Pyramids of Giza are mentioned in Vicat's work (Vicat, 1837), saying: *"The mortar which binds the blocks of the Pyramids, and more particularly those of Cheops, is exactly similar to our mortarsa[a] in Europe"*. From the Egyptian times up to the pre- Portland era we will follow the world wide spread knowledge of masonry constructions based on mixtures of lime and thermally treated clays[b].

In continuation from old Egypt constructions through the era of the Greeks and Romans builders, we can follow Vicat work and in accordance with him see the variation of calcareous "cements". In Rome, the first book about architecture appeared written by Fussitius. His successors were Terrenius Varro, Publius Septimus, and lastly Vitruvius Pollio (1837), the last of whom said about his work that it contained all: *"that the Greeks knew of the art of building"*.

Alberti and Palladio in the fifteenth and sixteenth centuries described the methods of building concrete walls. Unfortunately, there is little information on the successful building technique in written form in the 17th century, whereas the beginning of 19th century offers a variety of written evidence also from experiments conducted in the 18th century. W. J. Dibdin (1882) described the "English cement" application in a recapitulation of the important works: *"Among the works of note, constructed in more recent dates wherein concrete was used may be mentioned the Millbank Penitentiary in 1811, constructed by Sir Robert Smirke; the Graving Dock and Sea Wall at Woolwich (1835) by Ranger"*. The published

[a] Chapter III: On Artificial Hydraulic limes, pp. 21–22 (Vicat, 1837): *"We usually take twenty parts of dry clay, to eighty parts of very rich lime, or to one hundred and forty of carbonate of lime. But if lime or its carbonate should already be at all mixed (with clay) in the natural state, then fifteen parts of clay will be sufficient."*
[b] According to the composition of calcareous sediment heated together or separately as experimentally proved and published in International Journal of Architectural Heritage (Hanzlíček et al., 2012).

knowledge of the most interested circle of engineers – the French Army officers – and the translations of their written works into English by an American Army officer and also a translation of Vicat's work on the subject (hydraulic mortars and cements) by the British Army leads to the conclusion that the quality of Roman mortars and cements was still a big secret for builders at the beginning of the 19th century.

First of all, it is necessary to understand the labeling of different forms and types of materials studied and used by French Army officers, the German chemist Mr. John from Berlin and the American and English engineers and translators of the French texts. The articles from the beginning of 19th century and all direct citations are presented in their original transcriptions.

The use of the word *cement* is directly linked to the Latin "caementum" – meaning stone or stoned. The word "concrete" means a mixture of hydraulic mortar, pebbles and sand. The definition by French General Troussart (1838a) was published in March 1838: *"Concrete is nothing else than masonry made from hydraulic mortar and small stones"*

What is very important is an understanding of the expressions "puzzolanas" by Treussart or "pouzzolanas" by Vicat, or "arena fossitia" and its special appearance "Puteol's powder" by Vitruvius. We have to understand that also the expression "arenas" is used frequently by all of the experts of the 19th century.

Vicat (1837) presented this explanation on p. 48 (in Section II, Chapter VI: Of the Materials Which Are Added to Lime, in the Formation of Mortar or Calcareous Cements): *"Pouzzolana, properly so called, is a volcanic matter, pulverulent, of a violet red colour, first dug out of the earth by the Romans near the town of Pouzzol, not far from Vesuvius."*

And on the page 49, he continued (Vicat, 1837): "The pouzzolanas are essentially composed of silica and alumina, united with a small quantity of lime, potash, soda, and magnesia. Iron is associated with them mechanically, in the magnetic state".

A Manual on Lime and Cement by A. H. Heath (1893), edited by E. & F. N. Spon, described pozzolana as "…a volcanic ash,… partly powder, partly coarse grained, or like pumice stone scoriae or tufa stone, and the colour ranges from white, whitish gray, blackish gray, brown, to violet red" .

M. Petot (1838), one of the French experts presented the following definition in the Journal of the Franklin Institute (JFI), May 1838: *"Puzzolanas may be arranged in two principal classes, namely, natural puzzolanas, and artificial puzzolanas. Among the first, the most energetic are, generally, volcanic matters of a composition analogous to clays."*

The artificial puzzolan was of great interest to all of the experts, and the best result was presented by General Treussart (1838b) with his essays on the burning of white clay from the deposit close to Cologne (used in the 19th century for the production of pipes). The burning was managed at moderate temperature. We read in Chapter VIII, Manufacture of Artificial Pouzzolanas by Vicat (1837) on p. 58: *"The agent employed is heat"*.

And the English translator's note at the bottom of page 59 (Vicat, 1837): "… to try the effect of the powder of some broken pieces of a vessel for containing water, made of porous biscuit manufactured from the same clay; and I was much surprised to find it nearly equally energetic with that which had been fresh calcined… We may therefore conclude, that artificial pouzzolanas of this kind are not materially injured by moisture, a fact which greatly enhances their value; and this observation is in correspondence with the experience of General Treussart who says (p. 123): 'As to artificial tarras, when once it has been prepared it requires no further care; for neither the action of the air nor humidity deprive it of any of its properties."

Vicat (1837) presented in the section on Artificial Pouzzolanas: "Under this denomination we shall include the clays, arenes, psammites, and shists [German term for slate], properly calcined; smithy slag, the refuse of the combustion of turf and coal, and pounded earthenware; and, lastly, tile and pot shards." on p. 49 (bottom).

How to understand Vitruvius': "arena fossitia"? Vicat (1837) described **Arenes** on page 46: "This is a sand, generally quartzose, with very irregular, unequal grains, and mingled with yellow, red, brown, and sometimes white clay, in proportions varying from one to three-fourths of the whole volume."

The expression "most energetic" and some others used later could be explained by Vicat's definitions in Chapter VII, Of the Qualities of the Different Materials Which Are Joined with Lime in the Fabrication of Mortars, or Calcareous Cements. (pp. 52–53) (Vicat, 1837): In what follows, we shall term every substance '**very energetic**,' which, when kneaded to a clayey consistency with very rich lime, slaked by the ordinary process, forms cement or mortar capable, 1st, of **setting** from the first to the third day after immersion; 2nd, of acquiring after one year the hardness of good brick; 3rd, of yielding a dry powder under the spring-saw…"

2nd. We shall call merely '**energetic**' every substance which, under the same circumstances as before, will produce a cement or mortar capable, 1st, of setting from the fourth to the eight day; 2nd, of acquiring, after a year's immersion, the hardness of a very soft stone; 3rd, of yielding a moist powder with the spring-saw.

3rd. We shall call every substance '**feebly energetic**,' which, under the same circumstances as before, produces a cement or mortar which, 1st, will set from the tenth to the twentieth day; 2nd, which acquires, after a year's immersion, the hardness of dry soap; 3rd, which clogs the saw."

4th. Lastly, we shall say that a substance is '**inert**,' when its presence in proper proportions in rich lime in

Table 1 The proportion of lime/clay in different type of mortars

From those times, we could recognize: "Plastic cements"	lime wt. %	clay wt. %
English cement – carbonic acid deducted	55.4	44.6
Cement of Boulogne pebbles	54.00	46.00
Pouilly Cement	42.86	57.14
The same –second variation	36.37	63.63
Russian cement	62.00	38.00
Cement of Baye	21.62	78.38

paste makes no alteration whatever in the manner in which the lime would behave, if immersed without mixture."

And Vicat (1837) continues (lower on p. 53):

"These definitions being fixed, we establish as the result of experiment,

1st. That the sands, properly so called, are generally '**inert**' substances.

2nd. The arenes, the psammites, and the clays, are generally '**feebly energetic**', and rarely '**energetic**' materials.

3rd. The pouzzolanas, natural or artificial, may be '**very energetic**,' or '**simply energetic**,' or '**feebly energetic**'."

The quantity of "energy" was then reduced to the rate of setting after immersion, which we could estimate, because this expression could nowadays be replaced by "activation" of the clayed substances by a corresponding heat.

In all of the cited works from the 19th century, we have found a wide range of materials and different techniques used (burning in airy conditions, burning in closed vessels, diverse types and techniques of slaking, various types of mixtures) but all of the tests and essays follow one target: to obtain stabile hydraulic mortar despite the materials on the construction site being different.

In this connection, Vicat (1837) stated in Chapter X, Of Calcareous Mortars or Cements Intended for Immersion, in the segment on Choice of Proportions on p. 68: *"……every builder ought to study the materials at his disposal"*. And his opinion is emphasized by: *"There is nothing in the physical characters, either of the arenes, the psammites, or the clays, which will enable us to prognosticate with entire certainty, what their action on rich lime will be."* (on p. 54 in Chapter VII)

We can see how difficult and sometimes controversial the situation of responsible experts was in the determination of the materials and the ratio of their proportion in the mass. There are numerous signals and notes about the importance of the alumina–silica rate, such as e.g. in the case of "aqua-fortis cement" (cement resistant to the influence of acids; the expression comes from French) mentioned in various works (Vicat, 1837; Heath, 1893): "*The remarkable cement known by the name of the '**aqua-fortis cement**' is nothing more than a combination of argil and potash, resulting from a very feeble calcination of nitre and moistened clay. It is a very energetic pouzzolana, but very dear.*" (Vicat, p. 63)

Nowadays, we understand better the effect of aqueous alkalis on thermally treated clay. We can apply ^{27}Al MAS NMR analyses on the sample of "activated" clay and, according to the work first published by Sanz et al. (1988), recognize the shift in aluminum ion coordination. We have also learned that only in five-fold and four-fold coordinated aluminum, could the ions be hydrated and that in alkali aqueous conditions they form a 3D net with silicon. Its negative charge as a consequence of its coordination change is balanced by alkalis. In the case of "aqua-fortis cement" with potassium; in other cases of these types of cements, with calcium as shown below:

The so-called **"common cement"**, described by M. Courtois, Engineer of Roads and Bridges, Paris (1834) and translated into English in 1838, published in the Journal of the Franklin Institute (June 1838) declares (Courtois, 1838): *"Clay, as has been long known, gives, by calcination and pulverization, a cement that being mixed with fat lime in various proportions, forms mortar that hardens slowly under water, but which in time acquires a degree of hardness superior to that of hydraulic lime, either alone or mixed with sand, as we shall have occasion to show."*

Similarly, we can read in the JFI, May 1838 the definition of **cement of Baye** among the so-called group of **plastic cements** presented by Petot (1838), containing 21.62 wt. % of lime and 78.38 wt. % of clay. The other types were assigned by places of the material deposits with the only exception – the English cement fabricate from a principal deposit near the Thames. *"In 1802, similar stone was found on the sea shore at Boulogne, but in rolled pebbles, and in too small quantity to become an object of regular preparation,"* on which we are informed by the same source on p. 300 (Petot, 1838).

The variety and wide range of lime/clay proportions (see Table 1) on the one hand shows the possibility of different raw material use, but on the other hand it must be evident that there is no standardization of the mixture and also in heat application as we were informed above (Dibdin, 1882).

A. H. Heath (1893) and above-mentioned W. J. Dibdin (1882) described (see the time lapse of Vicat, Troussard (1838–37) and Heath (1893) – more than a fifty-year difference!) the **“Roman cement”** according to the patent of James Parker (1791). We can find this cement under the name of **“English cement”** but also named as **“Parker’s Cement”**.

The hundred years from the invention and more than sixty years after Portland cement was patented, these cementitious materials are still of high interest to builders. Parker’s cement used septaria nodules of the London clay dredged up off the Isle of Sheppey, the Hampshire coast, Folkstone. *“These septaria consist of a dark-coloured aluminous limestone traversed by veins – fissures filled with calcareous spar.”*

The May 1838 edition of the JFI in a report from M. Mallet to the Societé d´Encouragement declared that (Petot, 1838): “The stones are first broken into small fragments: then burned in a kiln as is commonly done with lime, at a heat sufficient to vitrify them; afterward reduced to powder by a mechanical or other operation.”

Nevertheless, Vicat (1837) described in Chapter XV, Of the Natural Cements, p. 112: “That which is in England very improperly termed Roman Cement… is nothing more than a natural cement, resulting from a slight calcination of a calcareous mineral, containing about 31 per cent. of ochreous clay, and few hundredths of carbonate of magnesia and manganese.”

In his research of natural cements, Vicat (1837) later on the same page informed that: “Very recently, natural cements have been found in Russia, and in France; we may compose them at once by properly calcining mixtures made in the average proportions of 66 parts of ochreous clay to 100 parts of chalk.” In the June 1838 edition of JFI, Courtois (1838) defined **hydraulic cement**: “The terms of the series composed of 7, 8, and 9 parts of clay, respectively mixed with 3, 2 and 1 parts of lime, give, by calcination, substances that do not slake: their colour is more or less reddish, according to the greater or less quantity of oxide of iron in the clay.”

From the cited works and described experiments by different authors from France and England, we can conclude that so-called natural cements are always a combination of calcareous matters with clay calcined at a moderate temperature. Once again, we have to point out the importance of temperature: even in the above-mentioned descriptions we can see the discrepancy between the descriptions of Vicat’s and Mallet’s technologies.

With all of the experiments performed by General Troussart and others, we tend towards the moderate heat and effect nowadays known as “clay activation” when the usual temperature is 750 °C with a time dwell of various hours. Evidently many works from the 18th and 19th centuries, in that context, look for the iron content and content of magnesium carbonates or oxides. Some authors who used ochreous clays were convinced of the important role of iron oxides while some others disagreed and presented results with light colored clays as for example General Troussart did.

The actually focus on alumina-silicate netting and on the formulation of geopolymer theory and practice seems be, in light of the presented citations, a new understanding of aluminum ion coordination in clayed substances when heated at moderate temperatures, but the practice and also the foresight of Vicat and others were adorable (see Chapter XVII, On the Theory of Calcareous Mortars and Cements, p. 138) (Vicat, 1837): *“We persist in thinking, as we have always maintained till now, that the lime in cements of natural or artificial pouzzolanas, as well as in cements formed with the uncalcined psammites and arenes, enters into chemical combination with theses substances.”*

Further in his cement recapitulation and the definitions of its different types, Vicat (in Section III, Chapter X, Of Calcareous Mortars or Cements Intended for Immersion) presents (Vicat, 1837): “*Every calcareous mortar or cement destined for immersion, and mixed beforehand as a matrix, with a certain quantity of stones, fragments, or rubbish, constitutes what is called a **beton**.”*

We could assume that all of the knowledge of clay–lime mixtures, the technology of their preparation, the technology of bridge and road constructions was very important at the beginning of 19th century but had two basic obstacles:

The first obstacle was in the relatively small group of experts which were able to combine and calculate the proportion of both main (clay and lime) components. As mentioned above in our quote of Vicat (1837), Chapter X, p. 68: *“...every builder ought to study the materials at his disposal”*, which he had specified by saying: “*moreover, it is proper to determine the proportions for every locality.”* (p. 22, ibid.)

We can imagine that the level of general construction knowledge was very low and the usual manner of housing was too simple. We assume that we are actually dealing with a small or very small circle of experts in the construction of important buildings, bridges and roads as well as harbors and fortresses mainly formed at military schools and therefore keeping certain “secrets” or “specific knowledge” as a part of the state’s important matters.

The second obstacle is also mentioned above: Not even the experts were able to tell whether local material will suit the constructions or not – the physical methods of qualifications were not sufficient and methods of determining the chemical behavior were used very frequently with hydrochloride acid only. Therefore, the uncertainty of results, the necessity of permanent study of the local material used for construction, and the search for the proper proportions and technology were later, when Portland cement appeared, the main reasons of the lapse of lime/clay combinations. The preparation of natural cements and artificial pozzolanas required not only specific experience and knowledge, but it was also very time consuming. The choice of a suitable raw material, lime burning and slaking are much more sophisticated than the simple use of standard Portland cement in an admixture with pebbles and water.

Portland cement (patented by Josef Aspdin in 1824) used similar materials like natural cement did, but the elevation of the temperature of burning up to the 1520 °C incurred clinkers with defined qualities. The simple admixture of powdered clinker with water and gravel provides everyone with the possibility to make his own *béton* or concrete with defined qualities. The Portland era significantly changed also the meaning of the word "cement". The original sense of binding material, or better and exactly "stone-like" material, was changed, and nowadays the word "cement" equals Portland cement.

Like in many other examples of a novelty – a new material, simpler to use and also yielding standard results totally – overcomes the old habits and knowledge.

In the second half of 19th century and specifically during the industrial development in 20th century up to the 1970s and 1980s, no one cared about the environmental impact of Portland cement production.

Scientists all over the world have since had a new scope of research. The formation of high-temperature products; di- and tri-calcium silicates (C_2S and C_3S) and the calcium aluminates (C_xA) and their hydrates were established as binding agents and matters responsible for concrete setting and hardening (Richardson, 1999; Scherer, 1999; Andersen et al., 2004). The burning temperature and binding precursor are responsible for the formation of the C-S-H gels in concretes; (sometimes also tobermorite was mentioned) made from Portland cements. The general acceptation of di- and tri-calcium hydration simulated therefore a similar reaction when silica is in contact with lime.

We can now point out that a temperature below 1000 °C, in historical works usually recognized as *"a very moderate roasting"* or *"[heating] to a point between a cherry red and forging heat"*, (Vicat, 1837), p. 58–59, means temperatures from 650 °C to 780 °C, (see a comparable measurement of bulb filament with kiln temperature) and hardly or never forms di-, tri-calcium silicates. The final products of moderate burning are of cause different; here we can cite from Chapter XI: Of Mortars Constantly Exposed to the Air and Weather, by Vicat (1837), p. 86: *"One thing which we know to be quite certain, and which we ought never to lose sight of, it this – that there is no sand whatever, be it red or yellow, grey or white, with round grains or angular ones, &c., which can, if it be inert, form a good mortar with rich lime."*

This opinion was also that of German chemist Mr. John from Berlin, who however: "was not long in discovering its insufficiency, by assuring himself by direct experiments, that caustic, and even boiling lime, has no action upon quartz" (Chapter XVII, p. 125) (Vicat, 1837).

We have two different situations, one supposing no action between quartz and lime and the other, which with high temperature action forms di- and tri-calcium silicates. Yet we have to add: There is a third possibility, which supposes the calcium ion acting on activated clay substances in aqueous conditions. In such a situation, there is a direct chemical bond between the calcium ions, having two positive charges and balancing two negatively charged aluminum ions in tetra-coordination to the oxygen. As we know, these aluminum ions are chained with silica and form amorphous alumina-silicates.

The scientific studies on these phenomena started at the beginning of the 1950s in Ukraine by professor Gluchovskij (1959) and his successor professor Krivenko (1992) and were focused on blast-furnace slag transformation by alkalization. The main target was to use these materials for constructions. Then, it is necessary to mention especially that the French, Spanish and Czech studies (Davidovits, 2008; Palomo and Fernández-Jiménez, 2007; Hanzlíček and Steinerová-Vondráková, 2002) and the newly translated (Davidovits, 1994; Hanzlíček, 2003) and interpreted work by Vitrivius with the identification of materials have reopened a new possibility for a big return – back to the natural cements, or actually so-called "geocements" and the specific use of clays in construction.

In a world in a post-industrial era and with better, scientific recognition, it is time to protect the environment and reuse natural cementitious materials. The moderate burning of clays does not produce any carbon dioxides, with the only waste being water vapors. The development in natural sciences and all types of modern analytical methods eliminates the uncertainty of pre-Portland era experts and scientists. Nowadays, we are able to calculate exactly and with precision the proportions of substances and guarantee the resulting quality of materials.

With a little nostalgia, we cite once again Vicat (1838), who wrote on p. 118: *"It is therefore Vitruvius whom we ought to consult, when we want to clear up any point of controversy regarding the architecture of the Greeks and Romans."* We of course completely agree, complementing this statement: It is necessary to properly understand all of the expressions used in Vitruvius' work and exploit the old knowledge for current purposes.

CONCLUSION

Very old builder's knowledge combining lime and thermally treated clay was rehabilitated on the beginning of 50^{th} of 20.century. The specific effect of temperature on clayed substances and understanding of the changes in aluminium coordination opened new field of studies. But "new" only in accordance with explanation not in previous and very old experience demonstrated by excellent example of "aqua fortis cement". The effect of alkali aqueous solution on thermally treated clay and the formations of alumina-silicate netting were proved in hundred scientific works. Presented recapitulation of different types of ancient and historical "cements" and "concretes" returns our attention from high energetic consumption and environmental pollution by CO_2 of Portland, back to the old, newly understood experience – the use of low temperature treated clays in aqueous alkali solutions.

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