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Preface

Writing a book on the chemistry of cement and concrete is a very responsible task, and if we take into account very valuable works of Lea and principally of Taylor, even unusually responsible. His last book is of the highest value and, apart from its clear presentation of all important problems of cement chemistry, it contains a different and interesting Taylor's hypothesis, among others concerning the structure of C-S-H phase.

The progress in cement chemistry was particularly very quick in the last thirty years, principally because of the development of new methods and techniques, including the progress in scanning electron microscopy and introduction of some non-typical, quite new methods. To the latter ones I enclose the electrons Auger, which make possible to determine the superplasticizer layer on cement grains. In my book, I tried to present the maximum of interesting experimental results and linked them with hypotheses, leaving for the readers the last choice.

One of my goals was also to remind some scientists, which innovative works make possible the further development of cement chemistry and which were forgotten, particularly by young researches. A typical example is Professor Hans Kühl, who already in 1907 had established the accelerating effect of sodium hydroxide and of sulphate ions on the hardening of granulated blastfurnace slag. In 1908 H. Kühl obtained a German patent for the production of supersulphated cement, based on his discoveries. During the workshop "$Ca(OH)_2$ in Concrete" J. Gebauer reminded that the concrete from this cement, used to build the Beervlei Dam in South Africa, had after forty five years of exploitation the strength of 124 MPa. The most probable is that only "the lime saturation factor", which was also introduced by H. Kühl, is till now linked with his name.

The writing of this book would not be possible without numerous fruitful discussions with my friends, whom I present my warmest thanks. I owe particularly many to the discussions with the following professors: A. Bielański, H. F. W. Taylor, F. W. Locher, W. Wieker, and A. Małecki, as well as to Sorrentinos and to Mike George.

Without crucial help of Professor Wiesława Nocuń-Wczelik, who translated the majority of the book, appearing of the English version will be not possible.

I present my thanks to my young assistant Aleksandra Bochenek, who wrote the English version of all tables and figures, as well as text edition, and particularly the preparation of figures was a very laborious task.

I would like also to thank my former co-worker Barbara Trybalska for the beautiful scanning electron microscope photos that she took me when she worked with me in the AGH University of Science and Technology.

Kraków, September 2013 Wiesław Kurdowski

Acknowledgments

In the book there are many figures which enhance its value in a significant degree and make several phenomena much clearer for the readers. All these figures are touching very important and, in majority of cases, complicated processes or relations and were included in the papers of world–known authors.

I would like to present my warm thanks for all authors as well as for the publishers, being copyrights holders, who granted me permission to reproduce these figures in the book. First of all, I address my thanks to Elsevier, because the majority of figures are from the great journal "Cement and Concrete Research", as well as to American Ceramic Society, Presses des Ponts et Chaussées and Applied Science Publishers. I address also my thanks to Editions Septima, which edited the Proceedings of 7th International Congress on the Chemistry of Cements in Paris in 1980. However, I could not find neither Editions Septima nor the successors of this Publisher. The same was with the Liaison des Laboratoires des Ponts et Chaussées Publisher, to which I address also my deep thanks. I due also my great thanks to Chemical Publishing Company, INC. to grant me permission to reproduce some figures from the excellent book of F.M. Lea "The Chemistry of Cement and Concrete". All these figures are of crucial importance for my book.

Contents

Chapter 1
Cement Kinds and Principles of their Classification

1.1 The History of Binders and Concrete

In the early period of civilisation the buildings were constructed by placing one heavy rock block on another, which were laying firmly due to friction forces only as like that of the famous edifices in Mycenae. With the civilisation development the different binders started to be used [1].

In Egypt the dried clay bricks without burning were linked with Nile slim (2). Such construction was effective in dry climatic zone only, because low moisture durability of these materials. Also the blocks in first stairs Djoser's pyramid were linked with clay (twentyseventh century before Christ) in Sakkara [2].

The plaster found wide application in ancient Egypt [2]. It was applied as mortar and to stucco decoration, for example in Tutankhamen's tomb, for finishing the tombstones of calcite (called alabaster). As mortar it was used in pyramids, in Giza. The beginning of its application is not establish; it is regarded that it falls in the period from 5,000 to 3,400 year before Christ [2]. The plaster application, instead of lime Jaworski explains by the lack of fuel, because the limestone are more easily accessible than gypsum raw materials [2].

The lime mortars were introduced to Egypt only about 300 year before Christ the Romans and the Greeks, which on turns did not know gypsum because of its limited usefulness in the humid climate of Italy and Greece.

The lime was applied very long ago by Greeks, and even earlier on Crete [2]. In turn from Greeks it was adopted by Romans. The correct technology of lime slacking and mixing it with sand. The mortar was mixed very carefully and compacted, which assured it a high density, thus to our times the edifices can be found in which inside the mortar non–carbonated calcium hydroxide is preserved [1].

Both Greeks and Romans knew the properties of some volcanic deposits, which finely ground and mixed with lime and sand give the mortars not only of higher strength, but also of higher durability on water influence, also of sea water [1]. Greeks applied for this purpose volcanic tuff from island of Santorin (known for to–day as Santorin earth), and Romans different raw materials and tuffs from the Neapolitan gulf. The origin of the best material was Pozzuoli (Puteoli) to whom the name was given pozzolana. Vitruvius writes about it: "There is a kind of sand,

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which in natural state has the extraordinary properties. It was discovered in a gulf in proximity of the Vesuvius mountain; blended with lime and broken stone hardens as well under water as in ordinary building" [1]. Probably also very long ago the Romans started to apply Rheine tuff, known as trass [1].

The Romans replaced also the natural pozzolana by the ground roofing–tiles, bricks and porcelain. Lea states that the name "cement" in the Late–Latin or Old–French languages was for the first time used to determine the materials which now are called artificial pozzolanas [1]. Later on this name was used for mortar produced from three components, and only recently the to–day mining was adopted.

To Romans we also owe the name "hydraulic cement" as they defined the binders hardening under water and thanks to the reaction with water [3]. Some blended materials, in order to better define their composition, was called pozzolanic cements.

There are proofs that already in buildings in Create the crushed ceramic pot-sherds (minoyen culture) were added to lime to give it the hydraulic properties [1]. On this basis the assumption was developed that Romans used firstly artificial pozzolanic materials, before they check the natural pozzolanas. Jaworski stats that in twelveth century before Christ Phoenician used hydraulic lime to mortar building the temple in Cyprus [2].Already about tenth century before Christ they used the bricks flour as the admixture giving to lime mortar hydraulic properties [2].

After the decay of Romans Empire the art of good binders production disappears. Lea cites the opinion of Viollet–le–Duc that in the period from nineth to eleventh centuries totally fell through the art of lime burning and it was applies as badly burned lumps, without the addition of crushed ceramic materials [1]. The quality of mortars became only improved in twelveth century, however, from fifteenth century their quality were already again very good, among others the washed sand, without clay impurities was used. There are proofs that in England from seventeenth century pozzolanas were again used. The mortars were still named cements which proofs can be found in Bartholomew Anglicus. However, the name "mortar" was also used already from the year 1290 [1].

During long time it was believed that the only one hydraulic binder is the mixture of lime with natural or artificial pozzolanas. It is proved by the Rondelet works on surprising level from 1805 and additionally, which underlines Lea, Rondelet cites the old authors, which were authorities, namely Pliny, Vitruvius, and saint Augustine [1]. The clarity of judgements, and also the extraordinary intuition of these authors surprises till today.

Revolution in the field of hydraulic binders production makes John Smeaton who made inquiries to the best material for the construction of the lighthouse in Eddystone Rock in 1756. He found that the better properties have the mortars of the lime burned from the raw material reach in clayey matter. It was equivalent to the discovery of hydraulic lime. Probably Smeaton was the first to use this name. Forty years later James Parker from Northfleet obtained a patent for the product from burned marl, which was named some years later as Roman cement. It was rapid setting cement. This cement started to be produced soon from the raw materials occurring near Boulogne.

The author of artificial hydraulic lime, produced by the burning of the interground mixture of choc and clay was L.J. Vicat, which published his results in 1818. He can be recognised as the predecessor of the technology of Portland cement production.

Joseph Aspdin is recognised as one of the inventor of Portland cement, which in 1824 patented the method of binder production from the burned mixture of limestone and clay, for the first time using the name Portland cement, because its colour resembled the stone from Portland. However, he burned the limestone at too low temperature, and the quality of product was bad.

Lea [1] and Bogue [3] state that the actual creator of Portland cement was Isaac Charles Johnson, which after several experiments established the correct proportion of clay and limestone, and also chose the advantageous, higher burning temperature. It happened at about 1845 year. It cannot be forgotten that he had taken advantage of the experiences of many his predecessors in England, chiefly J. Smeaton, Higgins, J. Parker and J. Frost, and also of Swede Bergmann, Dutchman J. John, and mainly L.J. Vicat.

Some authors claim that the higher burning temperature introduction we owe to Aspdin. Johnson applied this method in the factory in Gateshead, which he had taken after Aspdin leaved it in 1851 [4]. Johnson obtained a patent for improvement of Portland cement production in the year 1872. The Johnson achievement was recognised also by Michaelis, it is, however, the open matter to whom of two precursors of Portland cement producing—Aspdin or Johnson—this invention should be attributed [1, 4].

There are few information on the production of hydraulic lime in Poland. Górewicz states that it was used by the Teutonic knights for castle Malbork construction [5]. He states further the textile factory in Tomaszów Mazowiecki, which was build in 1828. The lime mortar was used for bonding of erratic boulders, from which the foundations were build. The significant importance ascribes Górewicz to the production, in the same period, of hydraulic lime used for the construction of Augustowski Channel. It was the hydraulic lime of excellent quality, and made of it mortars and concretes has today the compressive strength equal 15–50 MPa [5]. The hydraulic lime factory was erected in the neighbourhood of the foreseen channel location, and in the technology the advantage of L.J. Vicat works was taken [5]. During the production technology elaboration the experiments were made by professor Joseph Nowicki from Professional School in Warsaw.

Thirty years later the first cement plant on Polish Land was build in Grodziec and started production in 1857, which was the fifth working cement plant in the World (Fig. 1.1). In the twenty year of inter war period it was sell by the owner Stanislaw Ciechanowski to Solvay and significantly developed. In 1939 its capacity achieved 390 thousand tons per year [6].

Cement production on Polish Land increased quickly after the year 1884, and its development lasted till 1914. With exception of the small factory in Wejherowo, which was build in 1872, the remaining cement plants was erected after 1884 year—still in this year plant "Wysoka" in Łazy, in 1885 "Szczakowa" in Szczakowa and

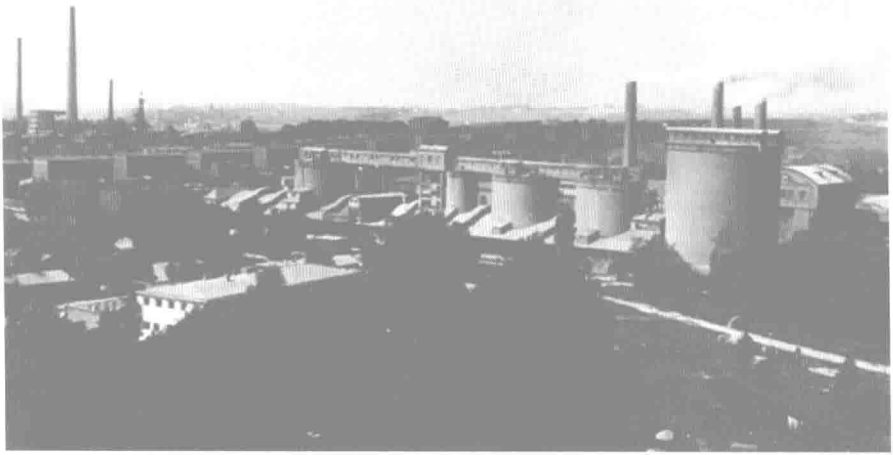

Fig. 1.1 Cement plant "Grodziec" in 1957, general view

"Bonarka" in Podgórze, near Kraków. In 1889 started the exploitation of "Goleszów" factory in Goleszów, and in 1894 "Firlay" in Lublin. During the years 1897–1898 further two cement plants were build, namely "Rudniki" near Częstochowa and "Klucze" near Rabsztyn. Very quickly further plants were erected, in total 15, but in this number the most ten in Russian Partition. During the First World War cement industry in Russian Partition was significantly destroyed, however, the remaining cement factories were not affected during war. From the year 1920 the progressive increase of cement production in Poland was noted, which, with the exception the crisis period, achieved a quick development (Fig. 1.2). The capacity was in year 1939 was equal 1.98 million, however the production was the highest in 1938 close to 1.72, due to the outbreak of the Second World War.

Cement from Poland was exported all over the world and was very well reputed. The new kinds of cement are introduced: high strength, with low heat of hydration [7]. As a curiosity can be reminded that people from cement plant "Saturn" patented the addition of siliceous fly ash to cement, which should increase the durability of concrete to sulphates.

After the Second World War there is a very quick development of cement industry in Poland. Already in the year 1948 cement production was higher than before the war, reaching 1.8 million ton and in 1955 was doubled, exceeding 3.8 million ton. The most tempestuous development period of cement industry was in the decennium 1965–1975, in which the production was increased from 8 to 16 million ton. The highest production was achieved in 1979, in which I was close to 23 million ton (Fig. 1.3).

Similar development was noted in others European countries and as an example cement production in Italy and Spain is given in Table 1.1, thanks to courtesy of

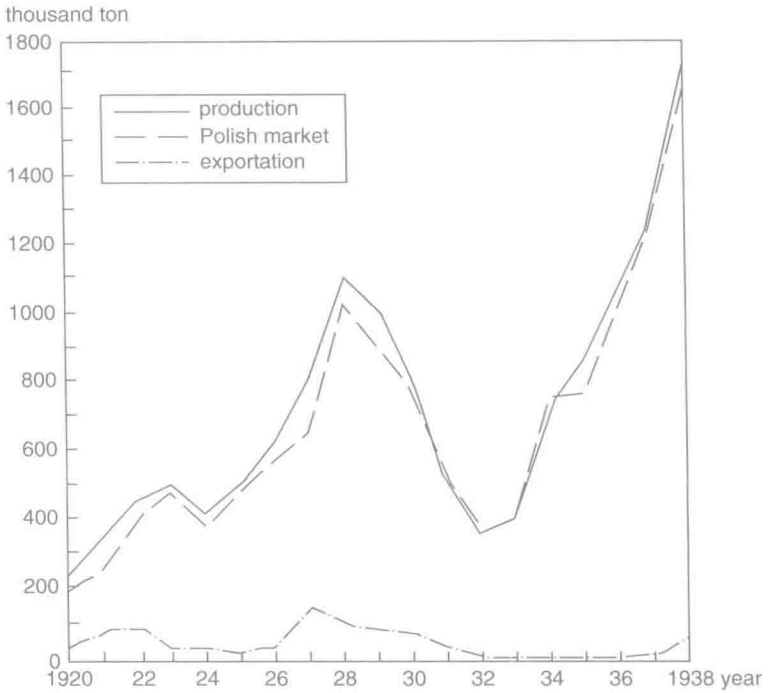

Fig. 1.2 Production and cement market in Poland in interwar period

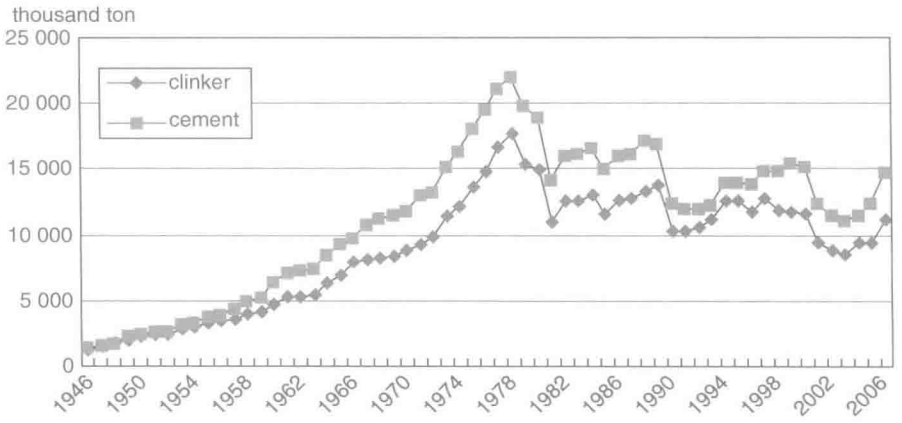

Fig. 1.3 Production of clinker and cement in Polish cement industry

Table 1.1 Cement production in Italy and Spain, thousand tone

Year	Italy			Spain		
1960	15.817					
		1964	22.935			
1965	20.733					
1970	33.126					
		1973	36.321		1973	22.247
1975	34.229			23.970		
1980	41.870			28.010	1978	30.230
		1981	42.996		1981	28.751
1985	37.266			21.880		
		1986	35.909			
1990	40.751			28.092		
		1994	33.084			
1995	34.019					
		1996	33.832			
2000	39.020					
2005	46.411					
2010	34.408					

Cement Associations of these countries. After 1980 significant fluctuations of cement production are typical, similarly as in Poland.

The economic crisis, which arrived in Poland after the 1979 embraced also cement industry. The quick decrease of cement market caused the diminution of its production (Fig. 1.3). The lowest level equal 14 million ton was in 1981, and after it was oscillating in the range from 15 to 16 million ton yearly. The change of political system in Poland brings the privatisation of cement industry, which takes place in the period from 1992 to 1998. The owners of about 90% of production capacity of cement industry became the big concerns, namely Lafarge, Heilderberg, Cement Roadstone Holding, Cemex and Dyckerhoff. This privatisation was very successful and resulted in cement industry as modernisation, the elimination of wet method and the reconstruction of almost all factories, with introduction of modern technical solutions. The kilns with precalciners, the roller press, closed circuit in cement grinding, with the application of the most modern separators. In cement plant "Chełm" the world unique technology of clinker burning, without raw materials grinding and in "Ożarów" plant the biggest kiln in Europe for dry method was erected, with the capacity of 8,000 tpd. Also in "Górażdże" and "Kujawy" the very modern technological lines on world level were introduced and there are only the most important solutions. Others numerous, not mentioned smaller modernisation, gave the lowering of energy consumption in industry by 25% and dust emission by 95%.

The concrete history is also of great antiquity. Basing on Lea definition [1], which names concrete as an artificial conglomerate of gravel or broken stone with sand and lime or cement, we can relate the beginning of concrete use by people with lime binder. Thus we do not relate to concrete the ancient buildings composed of the

aggregate bind with clay, but we will link the concrete with lime binder. The most ancient concrete elements based on lime are the Yiftah in South Galilean in Israel which are dated back to 7,000 year before Christ. They were discovered in 1985 and are described by Malinowski and Garfinkel [8]. This housing from Neolithic epoch embraces several buildings in which the floors and parts of walls were made of lime concrete with aggregate of crushed limestone. Malinowski and Garfinkel [8] state the vast concrete floors surfaces testify of the mass application of lime binder which proves the good knowledge of their production. The concrete production was also well known of which testify its good quality and measured compressive strength was in the range from 15 to 40 MPa and in one case was even 60 MPa [8].

The next examples of ancient concrete were found in Lepen Whirl, in Danube bend, in Serbia [9, 10]. They are linked with buildings, which origin is dated back to 5,600 year before Christ and are concerning also mainly the floors in the fishermen cabins.

The numerous concrete constructions are linked with Roman times, because in ancient Rome the technology of good lime mortar production was well developed, including also the hydraulic lime, which was applied for concrete production. Many such examples are described by Vitruvius, using the Greek term *emplechton* as a name of today concrete precursor, which was called in Rome *opus caementitium*. However, probably Greeks were the first which used hydraulic binders for concrete production. It was the mixture of lime with volcanic ash from Nisiros island, but also from Pozzuoli, from Greek colony in Italy, near Napoli. With this binder the pieces of stone were mixed and this concrete served among others for the production of water cisterns of the volume of 600 m^3 in Athena's temple, in Rhodes island and in Piraeus port. They were also described by Pliny [1]. Instead of stone pieces Greek used also the crushed tiles, among others in maritime constructions in Delos and Rhodes. The Romans adopted these knowledge from Greeks at about 300 year before Christ, and in production of hydraulic lime they used principally the tuff from Pozzuoli. The proofs of the durability of these materials are among others the numerous concrete constructions on the sea embankment between Napoli and Gaeta "polished by sea water, but not destroyed" [1]. Great Roman concrete construction retained to our times are Colosseum (82 year before Christ), Pantheon (123 year before Christ), theatre in Pompeii for 20 thousand spectators 75 year before Christ). The dome in Pantheon, with the diameter of about 44 m, was also made of concrete.

Also in North America the ancient concrete was found. Already in 1785 the ruin of El Tajin town, located in state Veracruz in Mexico, was discovered, but only during its reconstruction in 1924 the destructed concrete roofs in different houses were found [11]. The building of these houses in which the concrete roofs were applied are dated 1,000 year before Christ. This concrete, examined by Cabera et al. [11] appeared to be light concrete from hydraulic lime binder, and sand as well as aggregate were obtained from pumice (Fig. 1.4).

Hydraulic binder was produced by adding volcanic tuff to the lime, disintegrated to powder. Thus it became evident that the use of concrete in North America is dated to the same times as Roman buildings and the base of this composite was also lime with the addition of volcanic tuff.