poznan university of technology
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BUILDING MATERIALS – THEORETICAL BACKGROUND

Lab 3 – PROPERTIES OF HYDRAULIC BINDERS

Cement: determination of standard consistence, setting time, consistence of fresh mortar, flexural and compressive strength of cement (strength class)
Hydraulic lime: determination of flexural and compressive strength

European Standard

PN-EN 197-1:2012 Cement. Part 1: Composition, specifications and conformity criteria for common cements.
PN-EN 934-2+A1:2012 Admixtures for concrete, mortar and grout. Part 2: Concrete admixtures. Definitions, requirements, conformity, marking and labelling.
PN-EN 459-1:2015-06 Building lime. Part 1: Definitions, specifications and conformity criteria.

Terms, definitions and requirements

Cement – a hydraulic binder, i.e. a finely ground inorganic material which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability even under water.
Non-hydraulic binders are only harden in the presence of air. Hardening of non-hydraulic binder depends on its combination with carbon dioxide from the air (carbonation), by which it again becomes calcium carbonate (limestone).
Hydraulic binders require water to harden and develop strength.
Cement paste (grout) – cement that has been mixed with water. Usually the term implies that it has already become hard.
Mortar – a mixture of cement paste and sand used in thin layers to hold together bricks or stones. Technically, mortar is just a specific type of concrete with a small maximum aggregate size.
Concrete – a mixture of sand, gravel, and rocks held together by cement paste. The world's most widely-used man-made material.
Heat of hydration – the hydration reactions between cement and water are exothermic, meaning that they release heat. Large volumes of concrete can warm up considerably during the first few days after mixing when hydration is rapid.
Main constituent – specially selected inorganic material in a proportion exceeding 5 % by mass related to the sum of all main and minor additional constituents. Depends on the amount of main constituent two types of cement are distinguished: A: 6-20%, B: 21-35%.

Main constituents of cement:

a) *Portland cement clinker (K)* – is made by sintering a precisely specified mixture of raw materials (raw meal, paste or slurry) containing elements, usually expressed as oxides, CaO, SiO_2, Al_2O_3, Fe_2O_3 and small quantities of other materials. The raw meal, paste or slurry is finely divided, intimately mixed and therefore homogeneous. Portland cement clinker is a hydraulic material which shall consist of at least two-thirds by mass of calcium silicates ($3CaO*SiO_2$ and $2CaO*SiO_2$), the remainder consisting of aluminium and iron containing clinker phases and other compounds. The ratio by mass (CaO)/(SiO_2) shall be not less than 2,0. The content of magnesium oxide (MgO) shall not exceed 5,0 % by mass.

b) *Granulated blastfurnace slag (S)* – is made by rapid cooling of a slag melt of suitable composition, as obtained by smelting iron ore in a blastfurnace and contains at least two-thirds by mass of glassy slag and possesses hydraulic properties when suitably activated. Granulated blastfurnace slag shall consist of at least two-thirds by mass of the sum of calcium oxide (CaO), magnesium oxide (MgO) and silicon dioxide (SiO_2). The remainder contains aluminium oxide (Al_2O_3) together with small amounts of other compounds. The ratio by mass (CaO + MgO)/(SiO_2) shall exceed 1,0.

c) *Pozzolanic materials (P, Q)* – are natural substances of siliceous or silico-aluminous composition or a combination thereof. Although fly ash and silica fume have pozzolanic properties, they are specified in separate clauses Pozzolanic materials do not harden in themselves when mixed with water but, when finely ground and in the presence of water, they react at normal ambient temperature with dissolved calcium hydroxide ($Ca(OH)_2$) to form strength-developing calcium silicate and calcium aluminate compounds. These compounds are similar to those which are formed in the hardening of hydraulic materials. Pozzolanas consist essentially of reactive silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3). The remainder contains iron oxide (Fe_2O_3) and other oxides. The proportion of reactive calcium oxide for hardening is negligible. The reactive silicon dioxide content shall be not less than 25,0% by mass. Pozzolanic materials shall be correctly prepared, i.e. selected, homogenised, dried, or heat treated and comminuted, depending on their state of production or delivery.

   a. natural pozzolana (P) – are usually materials of volcanic origin or sedimentary rocks with suitable chemical and mineralogical composition.
   b. natural calcined pozzolana (Q) – are materials of volcanic origin, clays, shales or sedimentary rocks, activated by thermal treatment.

d) *Fly ashes (V, W)* – are obtained by electrostatic or mechanical precipitation of dust-like particles from the flue gases from furnaces fired with pulverised coal. Ash obtained by other methods shall not be used in cement that conforms to EN 197-1. Fly ash may be siliceous or calcareous in nature. The former has pozzolanic properties; the latter may have, in addition, hydraulic properties.

a. siliceous fly ash (V) –is a fine powder of mostly spherical particles having pozzolanic properties. It consists essentially of reactive silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3). The remainder contains iron oxide (Fe_2O_3) and other compounds. The reactive silicon dioxide content shall not be less than 25,0% by mass.
b. calcareous fly ash (W) – is a fine powder, having hydraulic and/or pozzolanic properties. It consists essentially of reactive calcium oxide (CaO), reactive silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3). The remainder contains iron oxide (Fe_2O_3) and other compounds.

e) *Burnt shale (T)* – specifically burnt oil shale, is produced in a special kiln at temperatures of approximately 800 °C. Owing to the composition of the natural material and the production process, burnt shale contains clinker phases, mainly dicalcium silicate and monocalcium aluminate. It also contains, besides small amounts of free calcium oxide and calcium sulfate, larger proportions of pozzolanically reacting oxides, especially silicon dioxide. Consequently, in a finely ground state burnt shale shows pronounced hydraulic properties like Portland cement and in addition pozzolanic properties.

f) *Limestone (L, LL)* – shall meet the following requirements:

a. The calcium carbonate ($CaCO_3$) content calculated from the calcium oxide content shall be at least 75% by mass.
b. The clay content shall not exceed 1,20 g/100 g. For this test the limestone shall be ground to a fineness of approximately 5000 cm^2/g determined as specific surface in accordance with EN 196-6.
c. The total organic carbon (TOC) content shall conform to one of the following criteria:
   i. LL: shall not exceed 0,20 % by mass;
   ii. L: shall not exceed 0,50 % by mass.

g) *Silica fume (D)* – originates from the reduction of high purity quartz with coal in electric arc furnaces in the production of silicon and ferrosilicon alloys and consists of very fine spherical particles containing at least 85 % by mass of amorphous silicon dioxide.

Minor additional constituent – specially selected inorganic material used in a proportion not exceeding a total of 5 % by mass related to the sum of all main and minor additional constituents. Minor additional constituents are specially selected, inorganic natural mineral materials, inorganic mineral materials derived from the clinker production process or constituents unless they are included as main constituents in the cement. Minor additional constituents, after appropriate preparation and on account of their particle size distribution, improve the physical properties of the cement (such as workability or water retention). They can be inert or have slightly hydraulic, latent hydraulic or pozzolanic properties. However, no requirements are set for them in this respect. Minor additional constituents shall be correctly prepared, i.e. selected, homogenized, dried and comminuted depending on their state of production or delivery. They shall not increase the water demand of the cement appreciably, impair the resistance of the concrete or mortar to deterioration in any way or reduce the corrosion protection of the reinforcement.

Additives – are constituents not covered as a main or minor additional constituent which are added to improve the manufacture or the properties of the cement. The total quantity of additives shall not exceed 1,0 % by mass of the cement (except for pigments). The quantity of organic additives on a dry basis shall not exceed 0,5 % by mass of the cement. These additives shall not promote corrosion of the reinforcement or impair the properties of the cement or of the concrete or mortar made from the cement.

Main cement types:

- CEM I Portland cement
- CEM II Portland-composite cement
- CEM III Blastfurnace cement
- CEM IV Pozzolanic cement
- CEM V Composite cement

Low heat common cement (LH) – common cement with a limited heat of hydration. Blastfurnace cement (CEM II) and pozzolanic cement (CEM IV) with high content of slag and ash belong to this group. It is used in a large, massive construction. That can prevent the occurrence of the ruptures and micro cracks in concrete.

Sulfate resisting common cement (HSR) – common cement which fulfils the requirements for sulfate resisting properties. It is used in concrete classified to exposure class of XA2 and XA3.

Calcium aluminate cement – is cement consisting predominantly of hydraulic calcium aluminates. Alternative names are "aluminous cement", "high-alumina cement" and "Ciment fondu" in French. They are used in a number of small-scale, specialized applications. Because of their relatively high cost, calcium aluminate cements are used in a number of restricted applications where performance achieved justifies costs:

– in construction concretes, where rapid strength development is required, even at low temperatures;
– as a protective liner against microbial corrosion such as in sewer infrastructure;
– in refractory concretes, where strength is required at high temperatures;

- as a component in blended cement formulations, for various properties such as ultra-rapid strength development and controlled expansion are required;
- in sewer networks for their high resistance to biogenic sulfide corrosion.

White Portland cement or white ordinary Portland cement (WOPC) – is similar to ordinary, gray Portland cement in all aspects except for its high degree of whiteness. Obtaining this color requires substantial modification to the method of manufacture, and because of this, it is somewhat more expensive than the gray product.

Standard strength of a cement – is the compressive strength determined in accordance with EN 196-1 at 28 days. Three classes of standard strength are included: class 32,5, class 42,5 and class 52,5.

Early strength of a cement – the compressive strength determined in accordance with EN 196-1 at either 2 days or 7 days. Two classes of early strength are included for each class of standard strength, a class with ordinary early strength, indicated by N, and a class with high early strength, indicated by R.

Strength class	**Compressive strength MPa**				**Initial setting time min**	**Soundness (expansion) mm**
	Early strength		**Standard strength**			
	2 days	**7 days**	**28 days**			
32,5 N	-	≥ 16,0	≥ 32,5	≤ 52,5	≥ 75	≤ 10
32,5 R	≥ 10,0	-				
42,5 N	≥ 10,0	-	≥ 42,5	≤ 62,5	≥ 60	
42,5 R	≥ 20,0	-				
52,5 N	≥ 20,0	-	≥ 52,5	-	≥ 45	
52,5 R	≥ 30,0	-				

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The family of common cements

Main types	Notation of the 27 products (types of common cement)		Composition (percentage by mass[a])										
			Main constituents										Minor additional constituent
			Clinker	Blastfurnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone		
						natural	natural calcined	siliceous	calcareous				
			K	S	D[b]	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM I	95-100	-	-	-	-	-	-	-	-	-	0-5
CEM II	Portland-slag cement	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	-	0-5
	Portland-pozzolana cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	-	0-5
		CEM II/B-P	65-79	-	-	21-35	-	-	-	-	-	-	0-5
		CEM II/A-Q	80-94	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-Q	65-79	-	-	-	21-35	-	-	-	-	-	0-5
	Portland-fly ash cement	CEM II/A-V	80-94	-	-	-	-	6-20	-	-	-	-	0-5
		CEM II/B-V	65-79	-	-	-	-	21-35	-	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	0-5
	Portland-burnt shale cement	CEM II/A-T	80-94	-	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B-T	65-79	-	-	-	-	-	-	21-35	-	-	0-5
	Portland-limestone cement	CEM II/A-L	80-94	-	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	21-35	-	0-5
		CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	6-20	0-5
		CEM II/B-LL	65-79	-	-	-	-	-	-	-	-	21-35	0-5
	Portland composite cement	CEM II/A-M	80-88	←12-20→									0-5
		CEM II/B-M	65-79	←21-35→									0-5
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	0-5
CEM IV	Pozzolanic cement[c]	CEM IV/A	65-89	-	←11-35→					-	-	-	0-5
		CEM IV/B	45-64	-	←36-55→					-	-	-	0-5
CEM V	Composite cement[c]	CEM V/A	40-64	18-30	-	←18-30→			-	-	-	-	0-5
		CEM V/B	20-38	31-49	-	←31-49→			-	-	-	-	0-5

[a] The values in the table refer to the sum of the main and minor additional constituents. [b] The proportion of silica fume is limited to 10%.
[c] In Portland-composite cements CEM II/A-M and CEM II/B-M, in Pozzolanic cements CEM IV/A and CEM IV/B and in Composite cements CEM V/A and CEM V/B the main constituents besides clinker shall be declared by designation of the cement.

Admixtures for concrete – material added during the mixing process of concrete in a quantity not more than 5% by mass of the cement content of the concrete, to modify the properties of the mix in the fresh and/or hardened state.

Water reducing/plasticizing admixture – admixture which, without affecting the consistence, permits a reduction in the water content of a given concrete mix, or which, without affecting the water content increases the slump/flow or produces both effects simultaneously.

High range water reducing/superplasticizing admixture – admixture which, without affecting the consistence, permits a high reduction in the water content of a given concrete mix, or which, without affecting the water content increases the slump/flow considerably, or produces both effects simultaneously.

Water retaining admixture – admixture which reduces the loss of water by a reduction of bleeding.

Air entraining admixture – admixture which allows a controlled quantity of small, uniformly distributed air bubbles to be incorporated during mixing which remain after hardening.

Set accelerating admixture – admixture which decreases the time to commencement of transition of the mix from the plastic to the rigid state.

Hardening accelerating admixture – admixture which increase the rate of development of early strength in the concrete, with or without affecting the setting time.

Set retarding admixture – admixture which extends the time to commencement of transition of the mix from the plastic to the rigid state.

Water resisting admixture – admixture which reduces the capillary absorption of hardened concrete.

Set retarding/water reducing/plasticizing admixture – admixture which produces the combined effects of a water reducing/plasticizing admixture (primary function) and a set retarding admixture (secondary function).

Set retarding/high range water reducing/superplasticizing admixture – admixture which produces the combined effects of a high range water reducing/superplasticizing admixture (primary function) and a set retarding admixture (secondary function).

Set accelerating/water reducing/plasticizing admixture – admixture which produces the combined effects of a water reducing/plasticizing admixture (primary function) and a set accelerating admixture (secondary function).

Viscosity modifying admixture – admixture incorporated in concrete to limit segregation by improving cohesion.

Lime				
Main areas of application				
Steel industry	Chemical industry	**Building**	Environmental protection	Agriculture
Building lime				
Air lime		Lime with hydraulic properties		
Calcium lime (CL)	Dolomitic lime (DL)	Formulated lime (FL)	Natural hydraulic lime (NHL)	Hydraulic lime (HL)
quicklime (Q)	quicklime (Q)			
hydrated lime (S, S PL, S ML)	hydrated lime (S)			
	semi-hydrated lime (S1)			

Lime – calcium oxide and/or hydroxide, and calcium-magnesium oxide and/or hydroxide produced by the thermal decomposition (calcination) of naturally occurring calcium carbonate (for example limestone, chalk, shells) or naturally occurring calcium magnesium carbonate (for example dolomitic limestone, dolomite)

Building lime – group of lime products, exclusively consisting of two families: air lime and lime with hydraulic properties, used in applications or materials for construction, building and civil engineering

Air lime – lime which combines and hardens with carbon dioxide present in air. Air lime has no hydraulic properties. Air lime is divided into two sub-families, calcium lime (CL) and dolomitic lime (DL). Air lime when appropriately batched and mixed with water, forms a paste that improves the workability (values of flow and penetration) and water retention of mortars. The carbonation of hydrates in contact with atmospheric carbon dioxide forms calcium carbonate which develops strength and contributes to the durability of mortars containing building lime (hence the name of air lime).

Calcium lime (CL) – an air lime consisting mainly of calcium oxide and/or calcium hydroxide without any hydraulic or pozzolanic addition.

Chemical requirements of calcium lime given as characteristic values						
Types of calcium lime	Designation	Values given as mass fraction in percent				
		CaO + MgO	**MgO**	**CO_2**	**SO_3**	**Available lime**
CL 90	Calcium lime 90	≥ 90	≤ 5	≤ 4	≤ 2	≥ 80
CL 80	Calcium lime 80	≥ 80	≤ 5	≤ 7	≤ 2	≥ 65
CL 70	Calcium lime 70	≥ 70	≤ 5	≤ 12	≤ 2	≥ 55

Dolomitic lime (DL) – is an air lime consisting mainly of calcium magnesium oxide and/or calcium magnesium hydroxide without any hydraulic or pozzolanic addition.

Chemical requirements of calcium lime given as characteristic values					
Types of calcium lime	Designation	Values given as mass fraction in percent			
		CaO + MgO	**MgO**	**CO_2**	**SO_3**
DL 90-30	Dolomitic lime 90-30	≥ 90	≥ 30	≤ 6	≤ 2
DL 90-5	Dolomitic lime 90-5	≥ 90	≥ 5	≤ 6	≤ 2
DL 85-30	Dolomitic lime 85-30	≥ 85	≥ 30	≤ 9	≤ 2
DL 80-5	Dolomitic lime 80-5	≥ 80	≥ 5	≤ 9	≤ 2

Forms of air lime:

a) Quicklime (Q) – is an air lime mainly in the oxide form (CaO) which reacts exothermically on contact with water. Quicklime is produced by calcination of the limestone in 900 – 1300 °C. Quicklime is available in a range of sizes from lump to powder.

$$CaCO_3 \rightarrow CaO + CO_2$$

b) Hydrated lime (S, S PL or S ML) – is an air lime mainly in the hydroxide form ($Ca(OH)_2$) produced by the controlled slaking of quicklime. Hydrated lime is available as: powder (S), putty (S PL) or slurry or milk of lime (S ML). Dolomitic lime is also produced as semi-hydrated dolomitic lime (S1), mainly consisting of calcium hydroxide and magnesium oxide.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Lime with hydraulic properties – building lime consisting mainly of calcium hydroxide, calcium silicates and calcium aluminates. It has the property of setting and hardening when mixed with water and/or under water. Reaction with atmospheric carbon dioxide is part of the hardening process. Lime with hydraulic properties is divided into three subfamilies, natural hydraulic lime (NHL), formulated lime (FL) and hydraulic lime (HL).

Natural hydraulic lime (NHL) – is a lime with hydraulic properties produced by burning of more or less argillaceous or siliceous limestones (including chalk) with reduction to powder by slaking with or without grinding. It has the property of setting and hardening when mixed with water and by reaction with carbon dioxide from the air (carbonation). The hydraulic properties exclusively result from the special chemical composition of the natural raw material. Grinding agents up to 0,1 % are allowed. Natural hydraulic lime does not contain any other additions.

Type of natural hydraulic lime	Available lime as $Ca(OH)_2$ %	Compressive strength MPa		Particle size % residue by mass		Setting times h	
		7 days	28 days	0,09 mm	0,2 mm	initial	final
NHL 2	≥ 35	–	od ≥ 2 do ≤ 7	≤ 15	≤ 2	> 1	≤ 40
NHL 3,5	≥ 25	–	od ≥ 3,5 do ≤ 10				≤ 30
NHL 5	≥ 15	≥ 2	od ≥ 5 do ≤ 15				≤ 15

Formulated lime (FL) – is a lime with hydraulic properties mainly consisting of air lime (CL) and/or natural hydraulic lime (NHL) with added hydraulic and/or pozzolanic material. It has the property of setting and hardening when mixed with water and by reaction with carbon dioxide from the air (carbonation). Depend on available lime as $Ca(OH)_2$ types of formulated lime can be distinguished as followed:

- FL A – ≥ 40% to < 80% of available lime as $Ca(OH)_2$;
- FL B – ≥ 25% to < 50% of available lime as $Ca(OH)_2$;
- FL C – ≥ 15% to < 40% of available lime as $Ca(OH)_2$.

Type of formulated lime	Compressive strength MPa		Particle size % residue by mass		Setting times h	
	7 days	28 days	0,09 mm	0,2 mm	initial	final
FL 2	–	od ≥ 2 do ≤ 7	≤ 15	≤ 5	> 1	≤ 40
FL 3,5	–	od ≥ 3,5 do ≤ 10				≤ 30
FL 5	≥ 2	od ≥ 5 do ≤ 15				≤ 15

Hydraulic lime (HL) – is a binder consisting of lime and other materials such as cement, blast furnace slag, fly ash, limestone filler and other suitable materials. It has the property of setting and hardening under water. Atmospheric carbon dioxide contributes to the hardening process.

Type of hydraulic lime	Available lime as $Ca(OH)_2$ %	Compressive strength MPa		Particle size % residue by mass		Setting times h	
		7 days	28 days	0,09 mm	0,2 mm	initial	final
HL 2	≥ 10	–	od ≥ 2 do ≤ 7	≤ 15	≤ 5	> 1	≤ 15
HL 3,5	≥ 8	–	od ≥ 3,5 do ≤ 10				
HL 5	≥ 4	≥ 2	od ≥ 5 do ≤ 15				