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Communication

The compressive strength of samples containing fly ash with high content of calcium sulfate and calcium oxide

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Abstract

Influence of composition of solid samples with fluidized bed combustion product, two types of cement binders and NaCl (as a chosen additive) on the compressive strength and the characteristics of microstructure of samples after 2 years of hardening were studied. NaCl causes marked increase of compressive strength after 28, 360 and 720 days of hardening. After 720 days of hardening the following detectable products of hydration are present in the samples: gypsum, portlandite, ettringite, hydroxylellestadite (Hexel — $Ca_{10}(SiO_4)_3(SO_4)_3(OH)_2$). Relationships between characteristics of X-ray diffraction analysis and compressive strength of specimens after 720 days were found.

Keywords: Solidification; Fly ash; Compressive strength

1. Introduction

Fly ash, produced as a by-product of classic combustion of ground coal, has been used in the building industry for a long time. Its parameters, for different fields of exploitation (lightweight concrete, admixtures to mortars, concrete, cement, ceramic clay mainly for brick production, etc.), are specified in the standards of many countries. Limited are mainly the sulfates and CaO content.

Fluidized bed combustion technologies use usually ground coal + calcite mixture for elimination mainly of oxides of sulfur. The content of sulfur compounds in coal may change and therefore also the contents of sulfates, calcite and its products in fly ash are not constant. The overwhelming amount of ash produced in this way has a markedly higher content of sulfates (mainly anhydrite) and CaO than limits allowed by the above mentioned standards. Therefore, they cannot be used for production of building materials and are usually stored in waste dumps in solidified form with or without a binder. The main advantage of those ashes is that they have very good binding properties without any supplementary activator.

The durability of the solidified structure of samples with high content of CaO, $Ca(OH)_2$, anhydrite or a Portland type cement binder may be limited when high content of sulfates is present in the sample or in the surrounding environment. Mainly hydrates of calcium sulfate and calcium sulfoaluminate compounds may be created in the samples. The declared danger of those hydrates is that their final volume may be markedly higher than the volumes of individual compounds before reaction. The growth of unfavorable tensions in the structure due to creation of the new formations mentioned may cause the gradual decrease of compressive strength and integrity of the solid structure. The leaching of hazardous compounds increases markedly from the solidified body in the waste dump when its structure is disintegrated. The potential utilization of the by-products mentioned in the building industry will be real only when all dangers mentioned will be excluded by research.

Our preliminary results showed that solid specimens prepared from fluidized bed combustion product + water stored 28 days in laboratory conditions had compressive strength of about 14 MPa. It rapidly decreased when the sample (after 28 days hardening in laboratory conditions) was stored in water. The structure had been destroyed after

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Table 1
Basic parameters of fluidized bed combustion product and result of leaching test

Volume weight (g/cm^3)	Density (g/cm^3)	Conductivity (mS/m)	pH (−)	Chlorides (mg/l)	Sulfates (mg/l)	PAH (ng/l)	Fluorine (mg/l)	PO_4^{3-} (mg/l)
Solid		Extract, solid/liquid = 1:10 after 24 h of standard leaching						
0.902	2.176	1193	12.65	150	1675	<26.2	3	10

PAH = polyaromatic hydrocarbons (12 pollutants).

several days. The decrease was stopped when cement without gypsum and NaCl were present in the sample. This observation is in accordance with results of publication [3]. They show that ettringite formation in the samples with $C_4A_3\bar{S}$ depends on several variables studied. The degree of linear expansion and the degree of reaction were markedly depressed when samples were stored in NaCl solution. Those results inspired our following experiments. Therefore, NaCl was used as an additive for depressing the ettringite formation and favorably influencing its morphology. A number of publications contain results of research concerning problems of ettringite formation and expansion and utilization of fluidized bed combustion products, as for instance Refs. [1–12]. In spite of this fact many problems have not been explained. One of the aims of our research is to broaden the knowledge concerning the microstructure and compressive strength changes of samples with bed combustion products and additives increasing the durability of specimens in conditions with high humidity or in water.

2. Experimental part

2.1. The aims of the tests

The main aim of the tests was to find proper binder and additive for securing the stability of solid structure of specimens containing fluidized bed combustion products stored in water. A further aim of the tests was to find relationships between composition of solid samples containing fly ash + different binder + NaCl, and their mechanical properties after 28, 365 and 720 days of hydration. The third aim was to determine the possibility of utilization of salts from incinerators as an additive to solidified specimens with fluidized bed combustion products.

2.2. Fly ash

The basic parameters of fly ash (fluidized bed combustion product) from a heating plant (Cinergy, Zlín, Czech Republic) are shown in Table 1. The results of X-ray diffraction analysis (apparatus Philips APD 15) are in shown Table 2. The content of the main compounds, using results obtained, was estimated (% b.w.) as follows: quartz = 6%, $CaSO_4$ II = 18%, hematite = 3.5%, CaO = 8.1%. Content of periclase, calcite, feldspar and portlandite was estimated up to 5%.

Table 2
Results of X-ray diffraction analysis of ash

Quartz	Hematite	$CaSO_4$ II	CaO	Calcite	Feldspar	Ca $(OH)_2$	Clays	Periclase
20.9	20.1	70.8	67.0	17.8	15.6	10.8	10.1	18.2

Characteristics of diffraction peak intensity, Ich, height of the peaks in number of division lines of the recording paper.

2.3. Cement

Two binders were prepared by grinding of clinkers, from two different cement works, in a laboratory ball mill (without gypsum). The contents of main minerals, determined by optical method (special microscope) are shown in Table 3. Clinkers used were chosen deliberately for markedly different C_3A content. Specific surface area of both binders was about 450 m^2/kg after Blaine.

2.4. NaCl

Two samples were tested. One was NaCl p.a. The second was the powder salt from the incinerator (Table 4). Very similar results concerning the influence of the salts on the compressive strength were obtained. The results presented in this article were obtained using NaCl p.a. for the better reproducibility of the parameters of samples tested.

2.5. Preparation of samples

Mixtures were prepared from fly ash, binder and water + NaCl using a laboratory mixer. Cubes with edge 25 mm were prepared. After 24 h of hardening the cubes were demolded and stored in conditions: temperature 21–23°C, humidity 80–90% up to 28 days. They were then immersed in redistilled water up to the time of determination of compressive strength after 360 days of hardening. The specimens, after 360 days of hardening, were stored under laboratory conditions in air. This method was chosen as a

Table 3
Composition of clinkers determined by optical microscopy

Compound	Cement S	Cement M
C_3S	67.00	77.21
C_2S	14.20	6.4
C_3A	10.1	1.15
C_4AF	8.6	15.02
CaO free	0.1	0.21
Total (%)	100.0	99.99

Table 4
Basic parameters of salt from incinerator

Parameter	Unit	Value
Weight loss 105°C	(%)	0.64
Ignition loss 950°C	(%)	0.81
NaCl content	(%)	89.1
Other soluble compounds, $\sum = 11$	(%)	0.9
Insoluble compounds	(%)	10.1

possible model in the practice when solidified samples in a waste dump may be cyclically immersed in water saturated by compounds leached from the solidified samples. Composition and parameters of samples are shown in Table 5.

2.6. Regression analysis

Computer program Statgraphics 2 (product of Statistical Graphic, USA) was used for determination of functional dependencies between tested dependent and independent variables. For judgement of every correlation significance the limits of Rd (Rd = R^2 — coefficient of multiple determination) were used [13]. Rd < 30% — bad or any correlation between tested variables exists, Rd = 30% to 60% — medium good correlation, Rd > 60% — very good correlation exists.

3. Evaluation of results

The results of regression analysis showed that very good correlation exists between the contents of compounds (X_i in Table 5) and the compressive strength of samples after different times of hardening. The chosen results in Figs. 1–4 show that compressive strength of samples increases proportionally with increase of cement and NaCl content and decreases with increase of water content. The compressive strength of the samples with cement M, with or without NaCl, is higher than that with aluminate type cement S. The proportional value of compressive strength C_s of samples with cement S (C_s with: C_s without NaCl) is larger in comparison with samples containing cement M. Similar courses of the same relationships as in Figs. 1–4 were obtained also after 360 and 720 days of hardening. The chosen results in Figs. 5 and 6 show that NaCl causes marked increase of compressive strength of samples with both types of cements after all tested times of hardening. This tendency was observed in the case of all modified samples in Table 5.

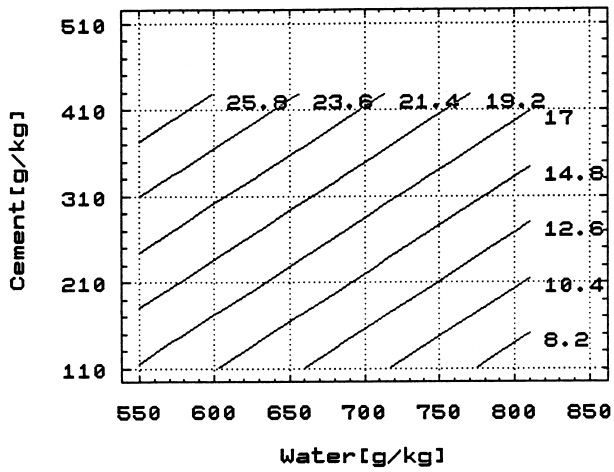

Fig. 1. Compressive strength (MPa — numbers in figure) versus cement and water content (g/1 kg ash) after 28 days of hardening. Cement S, NaCl = 0 g/kg.

The results presented above are illustrative. But they give only partial answers to the question as to which parameters and compounds cause increases or decreases of compressive strength. It seems that the results of X-ray diffraction analysis contribute to the answers.

Table 5
Composition of specimens in g/1 kg ash and their basic parameters

	Water X1	Cem. S X2	NaCl X3	28 days	360 days	720 days	C	E	G	P	H	Q
Sample No.	(g/kg)			(MPa)			Ich = characteristic of diffraction's intensity					
1	558	163	5.2	19.2	33.9	40.0	46	48	–	–	35	60
2	698	163	5.2	15.6	32.3	32.2	47	54	32	–	34	72
3 *	649	351	15.1	21.9	40.2	44.0	43	46	31	27	30	58
4 *	810	351	15.1	16.5	32.8	34.0	50	49	31	27	31	55
5 *	558	163	20.7	21.4	40.1	39.0	37	40	26	27	31	77
6 *	698	163	20.7	17.6	33.5	29.0	45	44	28	28	33	65
7	649	351	44.6	30.6	41.7	49.0	37	45	37	–	–	56
8	810	351	44.6	22.2	37.1	39.1	38	42	33	–	–	55
9 *	550	250	20.0	24.5	38.3	41	45	54	33	28	35	79
10	800	250	20.0	15.7	34.3	29.1	38	33	–	–	–	44
11 *	600	111	8.9	13.3	31	31.8	50	49	34	29	36	69
12 *	769	428	34.3	29	40.3	38.0	41	42	34	24	30	51
13 *	675	250	0.0	19.2	29.5	35.1	41	48	34	27	32	61
14 *	675	250	40.0	26.3	39.1	38.1	40	45	37	25	31	61
15 *	675	250	20	22.8	32.3	38.0	42	49	34	27	31	50

Cem. = cement, C = calcite 3.03 Å, E = ettringite 9.6 Å, G = gypsum 7.5 Å, P = portlandite 1.93 Å, H = Hexel 2.83 Å, Q = quartz 3.34 Å, Ich = characteristic of diffraction's intensity — number of division parts of recording paper.

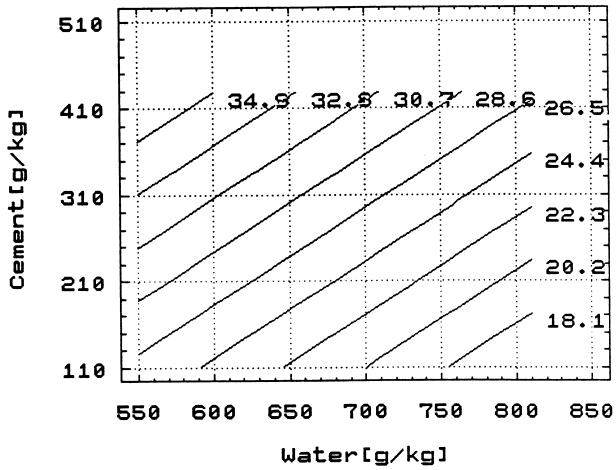

Fig. 2. Compressive strength (MPa — numbers in figure) versus cement and water content (g/1 kg ash) after 28 days of hardening. Cement S, NaCl = 40 g/kg.

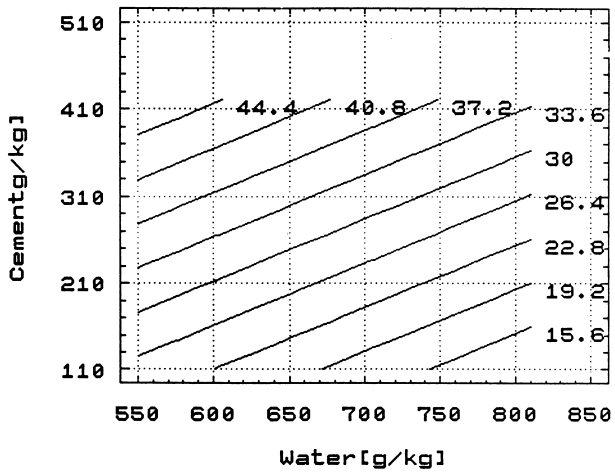

Fig. 4. Compressive strength (MPa — numbers in figure) versus cement and water content (g/1 kg ash) after 28 days of hardening. Cement M, NaCl = 40 g/kg.

The initial parameters of fly ash used are in Tables 1 and 2. The results in Table 2 indicate that the sample tested contains a residual amount of calcite. The main compounds, created due to the transformation of calcite and the chemical reactions in the process of combustion, are: anhydrite II, CaO and Ca $(OH)_2$. Those compounds may potentially react mainly with water and dissolved compounds and may create new formations whose influence on the solid structure may be positive or negative depending on various factors. They may also act as catalysts of cementitious properties of fly ash. The interpretation of X-ray diffraction peaks of samples (Table 5) was not simple because the differences between patterns were not distinctive. The samples contain mainly diffraction peaks of ettringite, calcite and quartz, which are distinctive. Less distinctive are those of gypsum portlandite and hydroxylellestadite. Diffraction of unhydrated clinker minerals 2.74 Å, 2.77 Å and the CSH*n* hydrated phase coincide with the diffraction of calcite. Therefore their quantitative identification is not possible.

The study of relationships between so-called macrostructural parameters of samples with cementitious binders, mainly mixing ratio of water, aggregate, binder, volume of air pores and compressive strength of samples after a certain time of hardening is the subject of many publications. Similar relationships between chosen main parameters are presented for instance in Figs. 1–4. The definition of relationships between the parameters presented by the results of X-ray diffraction analysis and compressive strength is much more complicated for several serious reasons. For instance, the intensities or parameters of certain diffraction peaks may be influenced by the phenomena of coincidence. Further, the relationship between content of a certain compound in the

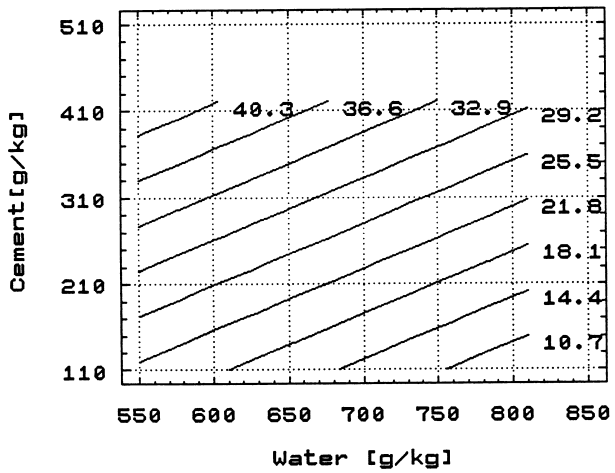

Fig. 3. Compressive strength (MPa — numbers in figure) versus cement and water content (g/1 kg ash) after 28 days of hardening. Cement M, NaCl = 0 g/kg.

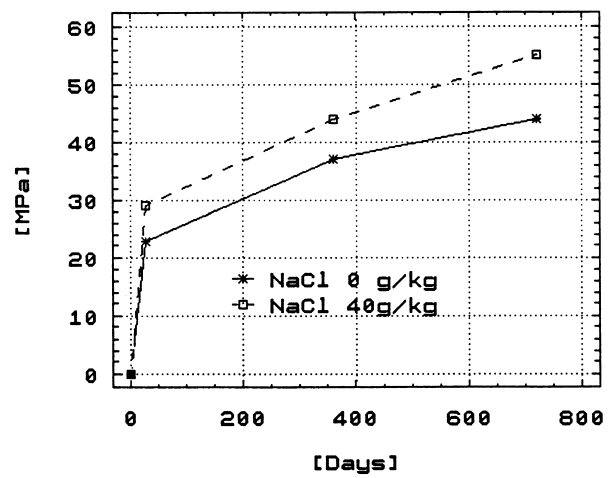

Fig. 5. Compressive strength versus time of hardening. Cement M. Composition see Table 5, Nos. 13 and 14.

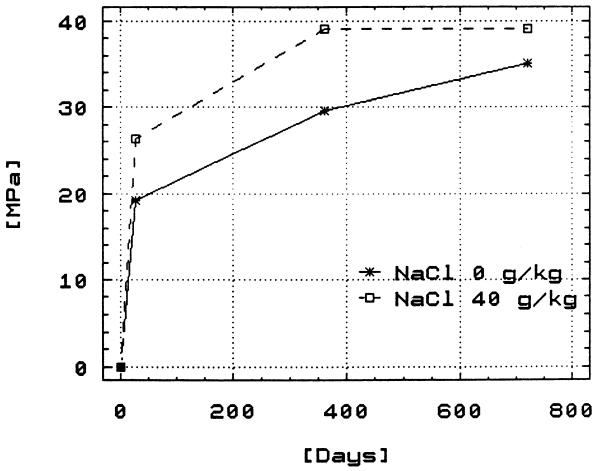

Fig. 6. Compressive strength versus time of hardening. Cement S. Composition see Table 5, Nos. 13 and 14.

sample and its corresponding diffraction parameter is usually not sufficiently precise. The identification and selective detection of certain (mainly amorphous) compounds, more or less influencing the compressive strength of the sample, cannot be reached by this method. Aware of those mentioned and also unmentioned problems, we made an attempt to find certain statistical characteristics between intensities of available diffraction peaks of compounds in Table 5 and corresponding compressive strength after 720 days of hardening. The number of series in Table 5 was reduced and only those having defined the diffraction peaks of all presented compounds were taken in account. Those 10 selected series are signed by an asterisk in Table 5. Regression analysis showed that a relatively good correlation exists between compressive strength and all diffraction characteristics in Table 5, when linear mathematical model is used ($R^2 = 66.26\%$). But other statistical characteristics (as t value and significance level of variables) indicated that the influence of one or more significant variables on the compressive strength changes was not taken into account. Subsequent analyses showed that correlation rapidly increases ($R^2 = 97.5\%$) when the dose of mixing water (influencing mainly the total porosity and the volume weight of specimens) is included in the number of independent variables. The results of further analyses showed that change in quartz diffraction intensities has minimal influence on the compressive strength because $R^2 = 96.28\%$ when this variable was excluded.

The results presented above indicate, if certain simplification is accepted, that a strength characteristic Sch (for instance the compressive strength) may be in the functional relation with a number of parameters defined approximately in Eq. (1):

$$\mathrm{Sch} = \sum_{i=1}^{n} X_i + \sum_{m=1}^{n} X_m. \quad (1)$$

X_i — macrostructural characteristics, mainly those influencing the final porosity of sample. The dose of mixing water seems to be the decisive variable belonging to this group in the case when the structural pores are removed by compaction (as is in our case).

X_m — parameters or characteristics of phase composition of the solid sample, mainly that of certain products of hydration. The number of new phases and their content after certain time of hardening depends mainly on the composition of solid compounds, on their proportional mixing ratio, time of hydration and hydrothermal conditions during storing.

The results of regression analysis in Table 6 provide the following two important results.

(a) Increase of calcite and ettringite (9.6 Å) content in the sample causes an increase of compressive strength. An increase of gypsum, portlandite, hydroxylellestadite ($Ca_{10}(SiO_4)_3(SO_4)_3(OH)_2$) and water content causes decrease of strength.

(b) The t values and significance levels of independent variables indicate that significance of influence (negative or positive) of independent variables on the compressive strength decreases in this order: water, hydroxylellestadite, portlandite, ettringite calcite and gypsum.

The change in phase composition of chosen specimens after different times of hydration is shown in Table 7. The following prevailing tendencies can be derived from data presented.

The entire amount of anhydrite II is transformed to gypsum up to 28 days of hardening. CaO is present only in dry fly ash. Part of it was transformed to $Ca(OH)_2$ in the process of combustion, cooling and storing (Table 7 — specimen 1) and the remaining part is transformed to $Ca(OH)_2$ during 28 days of hardening. Ich values of portlandite (Specimens 2, 3 and 4) have a tendency to decrease and that of calcite to increase. That may indicate that due to carbonation a part of portlandite is transformed to $CaCO_3$ during hardening. The presence of cement in Specimens 3 and 4 supports the increase of Ich values of quartz, calcite, ettringite and Hexel in comparison with Specimen 2.

More illustrative are the results in Figs. 7–9. The increasing rate of transformation of portlandite to calcite is favorable for increase of compressive strength as is shown in Fig. 7. Those results are in accordance with

Table 6
Results of regression analysis

Variable	Coefficient	t value	Significance level
Constant	196.7502	7.723	.00
Mixing water	− 0.08095	− 6.019	.00
Calcite	0.83909	2.863	.06
Ettringite	0.65443	2.957	.05
Gypsum	− 0.23355	− 0.865	.45
Portlandite	− 2.94285	− 3.249	.04
Hexel	− 2.69589	− 4.997	.01

Table 7
Characteristics of diffraction intensities Ich of chosen specimens

No.	Composition	Storing days	C	E	G	P	H	CaO	Anhydrite II	Q
1	dry ash	–	17.8	–	–	10.8	–	67	70.8	20.9
2	ash + water	28	27	40	40	57	–	–	–	–
3	Specimen No. 13, see Table 5	28	49	53	–	35	35	–	–	58
4		720	41	48	34	27	32	–	–	61

The symbols have the same meaning as in Table 5.

published relationships between the proportional content of both variables on the compressive strength of mortars with fine aggregate. The results in Fig. 8 show that growing ettringite content contributes to increase of compressive strength and that of Hexel supports the decrease of it. It is an interesting phenomenon because the ettringite formation in specimens with high content of sulfates has been connected with danger of deterioration. The results in Fig. 9 show that an increasing content of portlandite and gypsum causes decrease of compressive strength. Therefore, their transformation to calcite and ettringite seems to be advantageous for strength development.

The above presented results indicate that an increase of ettringite formation must not lead necessarily to the decrease of strength. The results in Ref. [3] confirm that Cl^- ions influence substantially the ettringite structure and its morphology. Its action resulted in the formation of thick stubby crystals instead of the usual elongated ones. Friedel's salt was also formed as a decomposition product of ettringite in the presence of NaCl. Those results were obtained by the study of pure $C_4A_3\bar{S}$ hydration. This short review indicates that further detailed research must be done for explanation of the mechanism of ettringite formation and its influence on expansion and cohesion of solid structure of samples containing fluidized bed combustion products.

4. Conclusions

(1) Compressive strength of specimens tested containing fluidized bed combustion products depends on the mixing ratio of compounds and composition of binder. Strength decreases with an increase of mixing water and increases with cement and NaCl content. The compressive strength of all samples increases proportionately with time of hardening up to 720 days.

(2) Under the same conditions the compressive strength of specimens with alite type cement is higher than that of specimens with cement having high content of C_3A.

(3) The results of regression analyses indicate that compressive strength after 720 days of hardening has a tendency to increase with increase of calcite and ettringite content in the specimens and to decrease with growing content of portlandite and gypsum.

(4) The results presented are valuable only for the conditions of the tests and materials used.

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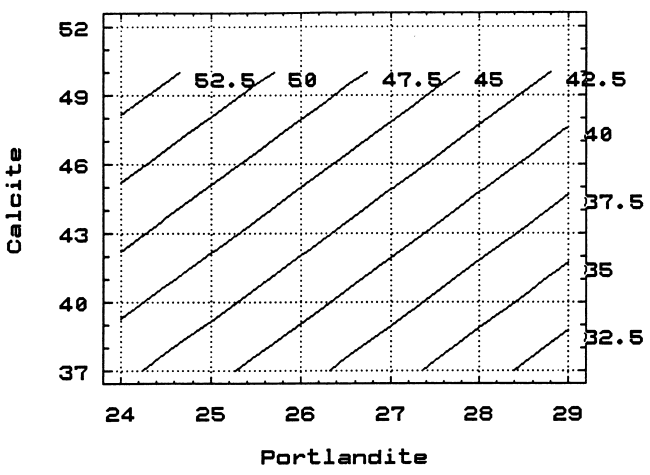

Fig. 7. Compressive strength (MPa — numbers in figure) versus Ich (number of division parts of recording paper) of calcite and portlandite when other variables are constant: water = 550, ettringite = 54, Hexel = 35.

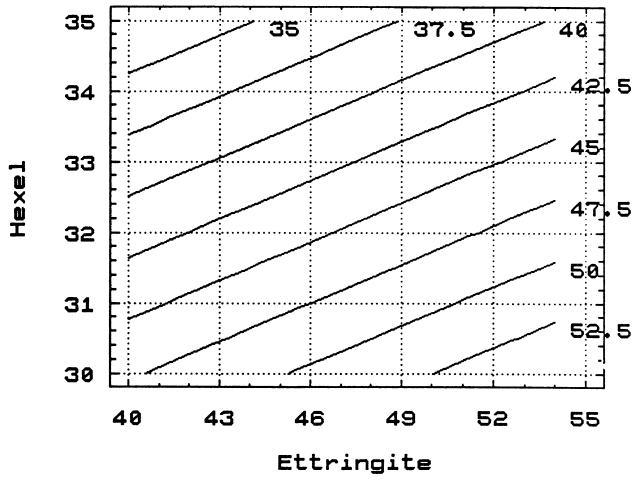

Fig. 8. Compressive strength (MPa — numbers in figure) versus Ich (number of division parts of recording paper) of Hexel and ettringite when other variables are constant: water = 550, calcite = 45, portlandite = 28.

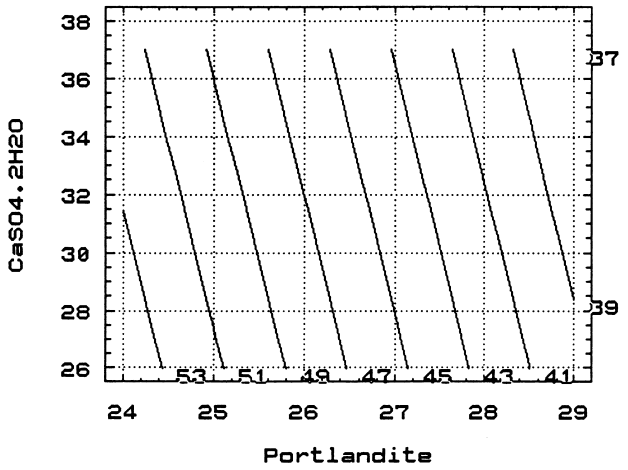

Fig. 9. Compressive strength (MPa — numbers in figure) versus Ich (number of division parts of recording paper) of gypsum and portlandite when other variables are constant: water = 550, ettringite = 54, Hexel = 35.

Pekárek from the Research Institution of Building Materials, Brno, for the interpretation of X-ray photographs.

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