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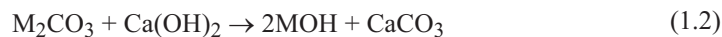
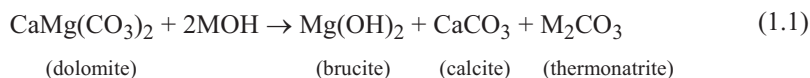
Alkali – carbonate reaction of aggregates

1. Introduction

1.1. Alkali – carbonate rock reaction and its occurrence

In 1957 Swenson and then Gillot I.E. (1964) and Duncan M.A.G. et al. (1973) described some of the carbonate rocks from Kingston in Ontario (Canada) which, when used in concrete, demonstrate destructive expansion. This process differed from the previously described by Stanton process of alkali-silica reactions and was characterized by the dolomite decay as an effect of its reaction with alkalis. Swenson named this process the dedolomitization reaction.

Even though many hypothesis on the process of alkali-carbonate reaction of aggregates have been created, most scientists believe that the process is as follows (Hadley 1961, 1964).



where:

M = K, Na or Li

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Dolomite undergoes dissolution due to its reactions with alkalis and creates calcite, brucite and alkali carbonate as products.

When the reaction occurs in concrete the natron may subsequently react with the milk of lime $\text{Ca}(\text{OH})_2$ creating sodium hydroxide NaOH and calcite CaCO_3 . This process leads to the recovery of alkalis and further dissolution of dolomite. Theoretically, the reactions occur until a complete dissolution of dolomite. In practice the products of dedolomitization reaction can react with other concrete components. For example, brucite $\text{Mg}(\text{OH})_2$ can react with silica creating hydrated sodium-calcium silica. This explains the absence of silica in the non-dolomitic limestones' reactive zones (Handley 1961).

Despite disagreements between authors on the mechanisms of the alkali-carbonate reaction of aggregates it is believed that, in some rocks, these mechanisms are responsible for initiating the expansion process (linear expansion) which leads to the concretes destruction (Góralczyk 2000).

1.2. Established goals and applied research methods

The following goals have been established:

- defining which aggregates, originating from carbonate rocks chosen for the tests, are reactive and then defining their mineralogical and chemical composition and their texture. This is all crucial in defining their utility when used in concrete production;
- defining the mechanisms of alkali-carbonate reactions in aggregates including mineral phase transformations and their impact on the size of expansion;
- verification of effectiveness and the possibility of implementing the mineralogical methods for the preliminary assessment of alkaline reactivity of the Polish carbonate aggregates.

In order to achieve the established goals, tests of alkaline reactivity have been conducted on representative samples of aggregates from carbonate rocks extracted from six different deposits. The tests have been conducted in accordance to the new method that have not been previously used in Poland: the ASTM C1260-94 and the so called "mortar-bar" method (Standard ASTM C1260-94). In order to examine the alkali-carbonate reaction phenomenon of aggregates, mineral phase transformations of reactive aggregates, and their impact on the size of expansion, mineralogical tests have been conducted on samples of aggregates before and after reacting with alkalis (solution 1N NaOH). This was conducted using the microscopy (polarization-OM method), X-ray diffraction (XRD) and electron microscopy (SEM) together with X-ray probe. The study results were compared with the existing knowledge and analyzed with the use of, among others, the method of statistical evaluation of results, including the correlational relationship, the comparative analysis method and descriptive analysis.

2. Materials – Aggregates

Samples of aggregates have been extracted from 6 different deposits listed in Table 1.

TABLE 1

List of deposits selected for study

TABELA 1

Zestawienie złóż wytypowanych do badań

No	Name	Symbol	Age (period)	Location	Type
1.	Bielawy	B	jurassic-oxford	Piechcin-Bielawy (Kuyavian-Pomeranian voivodeship)	dolomitized limestone, dolomite
2.	Dubie	D	devonian-givetian	Rudawa (Lesser Poland voivodeship)	dolomite
3.	Jaźwica	Ja	devonian-givetian	Jaźwica near Chęciny (Świętokrzyskie voivodeship)	limestone, dolomite
4.	Jurkowice	J	devonian-givetian	Jurkowice near Klimontowa (Subcarpathian voivodeship)	limestone
5.	Laskowa	L	devonian-givetian	Laskowa near Chęciny (Świętokrzyskie voivodeship)	dolomite
6.	Podleśna	P	devonian-givetian	Siewierz (Silesian voivodeship)	dolomite

3. Results

3.1. Results of the chemical composition studies

The results of the study on the chemical composition are demonstrated in Table 2.

All of the listed mineralogical, chemical and textural characteristics indicate that aggregates originating from the carbonate rocks from Dubie, Laskowa and Podleśna deposits should not cause the damaging expansion in concrete.

Samples of rocks from Bielawy, Jaźwica and, on a smaller scale, from Jurkowice are characterized by different mineralogical, chemical and textural qualities. In particular Bielawy meets all the criteria of mineralogical (content of SiO₂ and clay minerals), chemical (high content of units insoluble in HCl) as well as textural (low porosity, closed pores with a diameter of around 5 μm) composition typical for reactive aggregates demonstrating high expansion in concrete.

TABLE 2

Analysis of chemical composition of carbonate aggregates (content in wt.%)

No. and sample name	Parts undissolved in HCL	SiO ₂	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	Na ₂ O	K ₂ O	ignition losses	SO ₃	CaCO ₃	CaMg(CO ₃) ₂
	1	2	3	4	5	6	7	8	9	10	11	12
L	0.49	1.84	29.66	20.09	0.19	4.70	0.09	0.25	43.18	not found	52.97	42.02
P	7.84	5.17	33.09	13.52	3.19	3.38	0.09	0.13	41.43	not found	59.45	28.28
D	2.83	1.92	31.38	19.65	0.22	1.01	0.09	0.06	45.67	not found	57.83	41.10
J	0.94	0.70	48.90	4.29	0.29	1.96	0.17	0.10	43.59	not found	87.33	8.97
B	15.97	9.52	27.00	14.38	1.66	4.36	0.08	0.18	41.11	0.99	48.22	30.08
Ja	3.22	2.30	33.42	16.66	0.22	2.10	0.13	0.07	45.10	not found	59.69	34.85

TABELA 2

Analiza składu chemicznego kruszyw węglanowych (% mas.)

Aggregates from Jaźwica are characterized by a smaller percentage of admixtures that are believed to be the initiators of the damaging expansion processes, but in a quantity sufficient to indicate the potentially reactive nature of the rock.

Aggregates from Jurkowice, when looking at their chemical and mineralogical characteristics, seem harmless. Nevertheless, concern arises due to their distinctive texture, similar to the texture typical for reactive rocks.

3.2. Study results. Alkaline reactivity of carbonated rocks

The results of a study conducted using the ASTM C 1260 method and the “mortar bar” method demonstrated high values of linear change for Bielawy aggregates, exceeding the maximum of 3% (Table 3). Most of the samples had undergone partial or full disintegration.

TABLE 3

The maximum values of linear change of expansion in selected samples from studied deposits

TABELA 3

Maksymalne wartości zmian liniowych ekspansji poszczególnych próbek z badanych złóż

No.	Name	Sample No.	Max. value of linear changes, mortar – bar method [%]	Sample's evaluation	Max. value of linear changes ASTM C 1260-94 [%]	Sample's evaluation
1.	Bielawy	B – I	2.005	reactive	0.182	pot. reactive
		B – II	3.527	reactive	0.581	reactive
		B – III	2.161	reactive	0.388	reactive
		B – IV	0.577	reactive	0.089	nonreactive
2.	Dubie	D – I	0.0823	nonreactive	0.027	nonreactive
		D – II	0.1328	nonreactive	0.045	nonreactive
		D – III	0.1001	nonreactive	0.049	nonreactive
		D – IV	0.1303	nonreactive	0.038	nonreactive
3.	Jaźwica	Ja – I	0.0977	nonreactive	0.012	nonreactive
		Ja – II	0.1028	nonreactive	0.023	nonreactive
		Ja – III	0.1978	pot. reactive	0.027	nonreactive
		Ja – IV	1.8778	reactive	0.037	nonreactive
4.	Jurkowice	J – I	0.0201	nonreactive	–0.004	nonreactive
		J – II	0.1848	pot. reactive	0.004	nonreactive
		J – III	0.2067	pot. reactive.	0.011	nonreactive
		J – IV	0.0753	nonreactive	–0.011	nonreactive
5.	Laskowa	L – I	0.2228	pot. reactive	0.038	nonreactive
		L – II	0.1507	pot. reactive	–0.031	nonreactive
		L – III	0.0824	nonreactive	–0.023	nonreactive
		L – IV	0.0988	nonreactive	0.019	nonreactive
6.	Podleśna	P – I	0.0943	nonreactive	0.015	nonreactive
		P – II	0.0805	nonreactive	0.027	nonreactive
		P – III	0.1174	nonreactive	0.052	nonreactive
		P – IV	0.3512	reactive	0.019	nonreactive

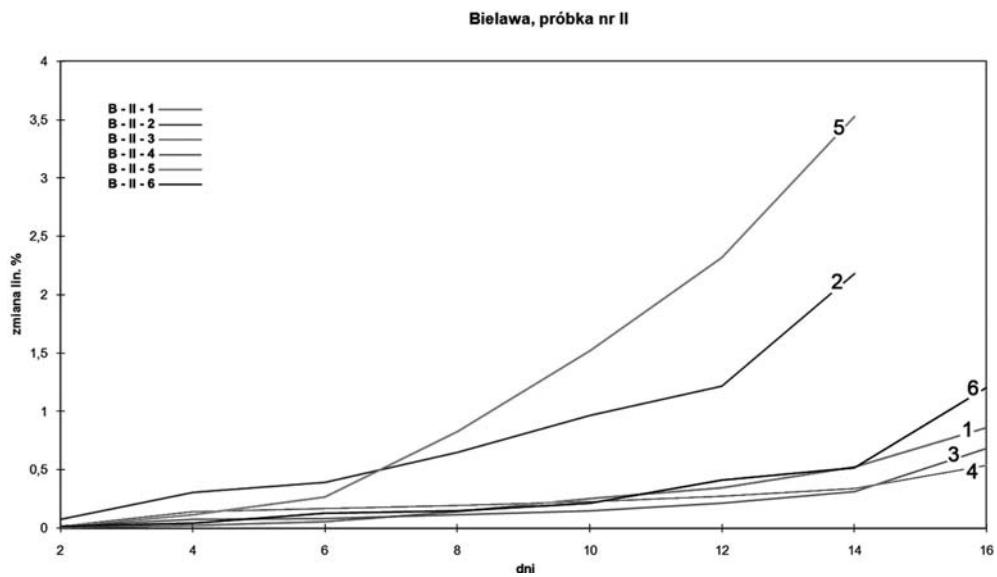


Fig. 1. Linear changes of aggregates according to the mortar bar method (Góralczyk 2000)

Rys. 1. Zmiany liniowe kruszywa według metody „prostokątnych beleczek ze skał” (Góralczyk 2000)

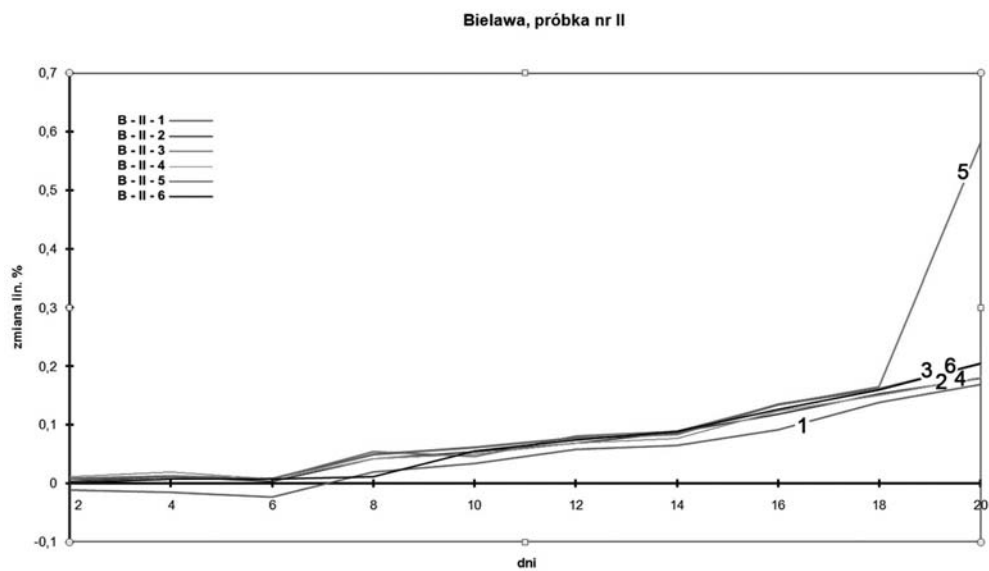


Fig. 2. Linear changes of aggregates according to the ASTM 1260-94 method (Góralczyk 2000)

Rys. 2. Zmiany liniowe kruszywa według metody ASTM C 1260-94 (Góralczyk 2000)

The expansive character of the Bielawy aggregates had been confirmed by reactivity studies according to the ASTM C 1260-94 method, as well as the results of studies with the use of SEM and XRD. The value of expansion of the tested mordant bars which are made of the Bielawy aggregates is demonstrated in Figure 1 and 2.

3.3. Mineralogical analysis of the samples of aggregates considered as reactive

Mineralogical studies conducted with various methods (OM, XRD, SEM) proved that permanent mineralogical and textural changes do occur in aggregate samples from Bielawy (including those used in concrete) defined as reactive and characterized as highly expansive (high values of linear changes). These are characterized by:

- A profound disintegration and its replacement (entire or partial), with fine-crystalline calcite $\text{Ca}(\text{CO}_3)$ (Phot. 2, 4), amorphous brucite $\text{Mg}(\text{OH})_2$ (Phot. 2) which reacts with silica forming hydrated silica which clusters in cracks and pores caused by expansion (Fig. 2, 4) and commonly occurring thermonatrite Na_2CO_3 (crusted, amorphous or fine crystalline). This has been confirmed by the results of XRD (Fig. 3, 4) and electron microscopy with the use of an X-ray probe (Fig. 5).

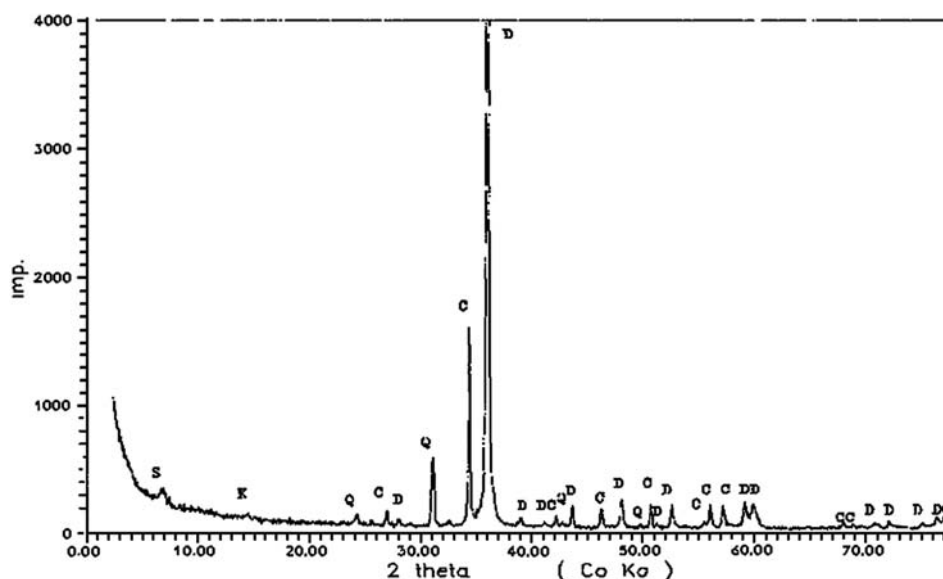


Fig. 3. X-ray pattern of Bielawy aggregates' sample (B-III-4) before the alkaline reactivity tests
 C – calcite, D – dolomite, K – kaolinite, Q – quartz, S – smectite (Góralczyk 2000)

Rys. 3. Dyfraktogram próbki kruszywa Bielawy (B-III-4) przed badaniem reaktywności alkaicznej
 C – kalcyt, D – dolomit, K – kaolinit, Q – kwarc, S – smektyt (Góralczyk 2000)

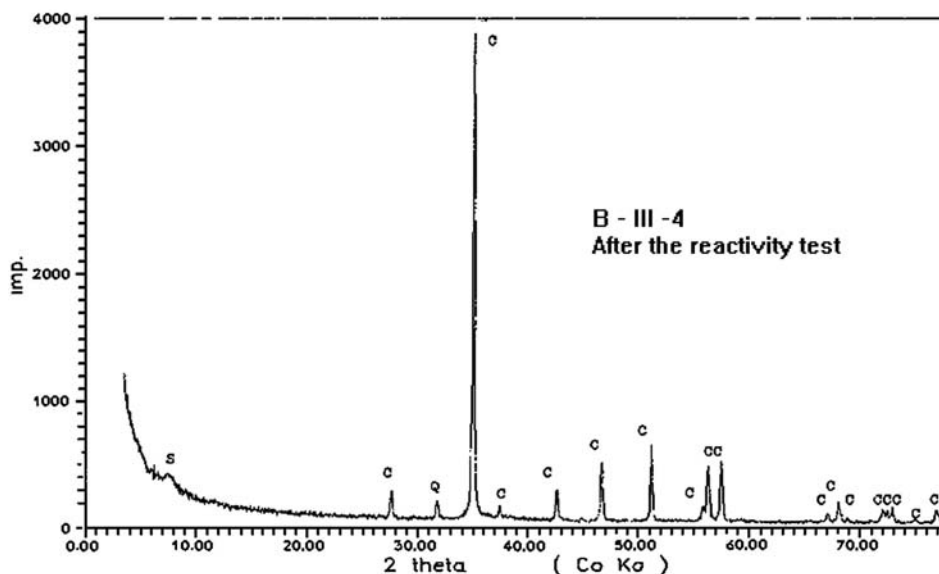


Fig. 4. X-ray pattern of Bielawy aggregates' sample (B-III-4) after the alkaline reactivity tests
 C – calcite, Q – quartz, S – smectite (Góralczyk 2000)

Rys. 4. Dyfraktogram próbki kruszywa Bielawy (B-III-4) po badaniu reaktywności alkaicznej
 C – kalcyt, Q – kwarc, S – smektyt (Góralczyk 2000)

- The formation of hydrated aluminosilicates of calcium, sodium and magnesium which are, most probably, the source of pressure that develops in rock pores as a result of their expansion (Phot. 2, 3).
- The formation of clear reactive zones around grains of dissolving dolomites with clear zonation deriving from the products of the above mentioned reactions.
- The formation of a distinctive texture with widespread cracks and pores that are usually filled with the products of the alkaline reactions (Phot. 2, 3).

Similar changes that indicate their reactive properties can be noticed in samples of mortars that contain reactive aggregates.

However there have been no alkaline reactions in samples defined as nonreactive and demonstrating no linear expansion. Mineralogical studies, particularly XRD tests, have shown that the mineralogical composition of aggregate samples are identical, before and after conducting the tests on alkaline reactivity. Typical products from the reaction, such as resulting from the decay of dolomite as well as thermonatrite, brucite and conglomeration of amorphous silica gel, do not occur. There are also no textural changes, such as cracks indicating expansion.

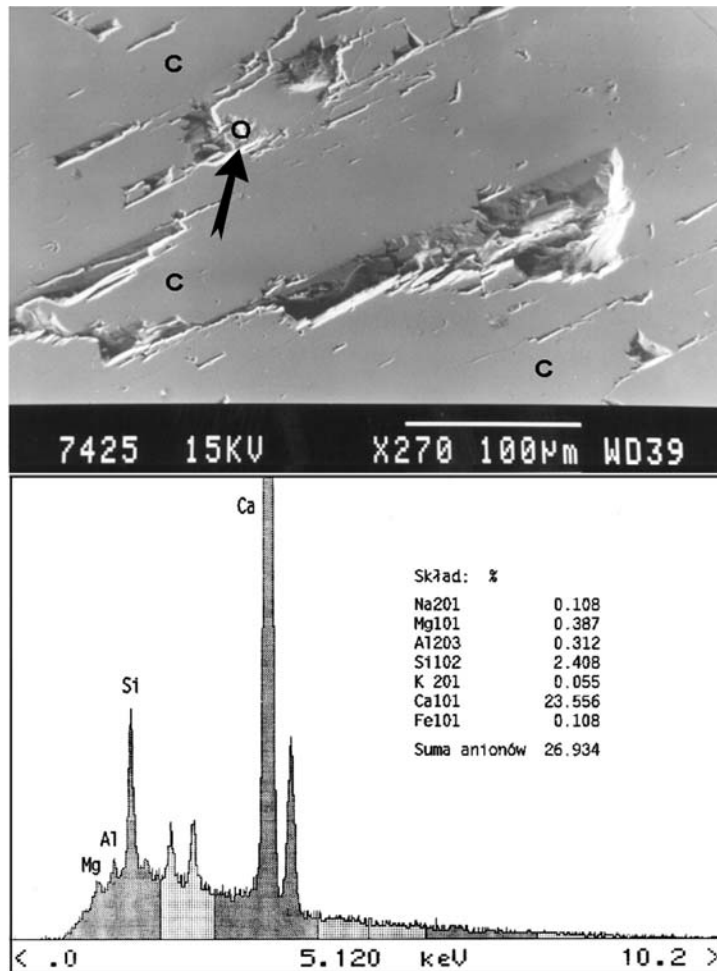
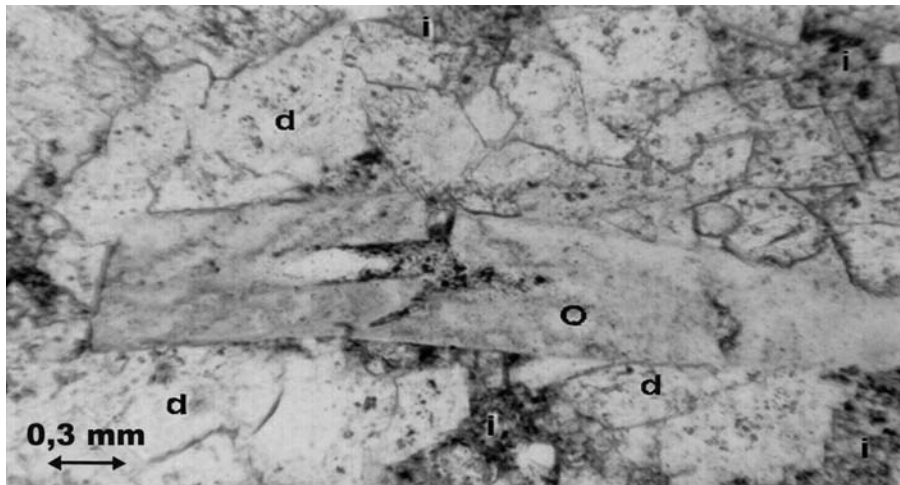


Fig. 5. SEM BSE and microanalysis EDS of Bielawy aggregates' samples (B-II-2) after testing the reactivity, in the range of calcite's secondary grain C – calcite in cracks with concentrated secondary clay-silica minerals (O) enriched with magnesium (Mg).

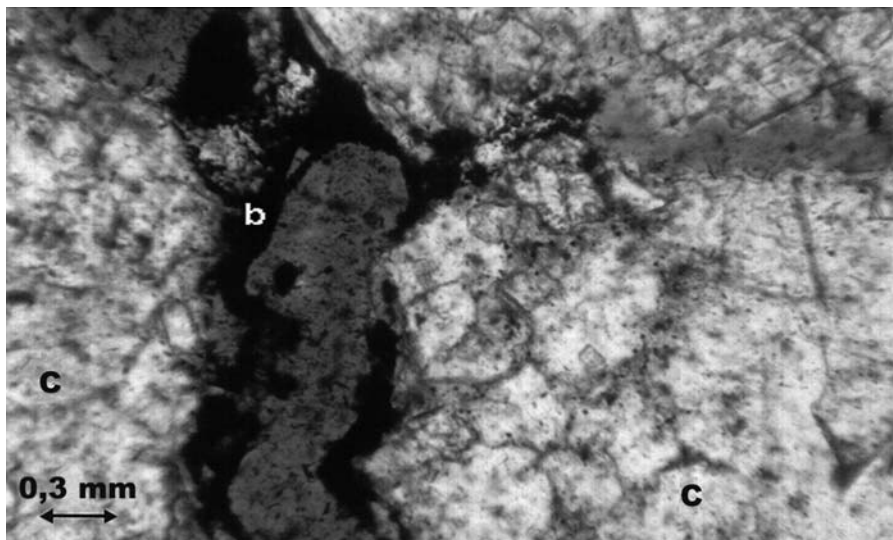
The arrow points at the place where the probe had been used (Góralczyk 2000)

Rys. 5. SEM BSE i mikroanaliza EDS próbki kruszywa Bielawy (B-II-2) po badaniu reaktywności, w obrębie ziarna wtórnego kalcytu C – kalcyt w szczelinach skupienia wtórnych minerałów ilasto-krzemionkowych (O) wzbogaconych w magnez (Mg).
Strzałką oznaczono miejsce wykonania sondy (Góralczyk 2000)



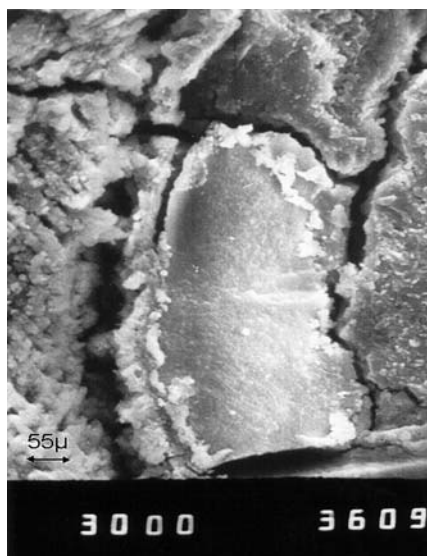
Phot. 1. Dolomite, medium and coarse-grained, Bielawy /B-I/
 d – dolomite grains, i – clusters of clay minerals, O – opaline silica
 1 polar. Sample before the reactivity tests (Góralczyk 2000)

Fot. 1. Dolomit średnio- i gruboziarnisty Bielawy /B-I/
 d – ziarna dolomitu, i – skupienia minerałów ilastych, O – krzemionka opalowa (igła gąbki)
 1 polar. Próbką przed badaniem reaktywności alkalicznej (Góralczyk 2000)



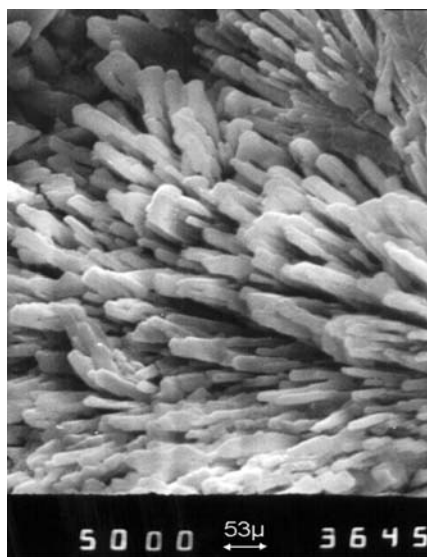
Phot. 2. Bielawy /B-IV-2/ Sample after the reactivity tests. Cracks system with black products of dolomitization process (clay-silica minerals, brucite) in the area of the secondary calcite grains C.1 polar (Góralczyk 2000)

Fot. 2. Bielawy /B-IV-2/ Próbką po badaniu reaktywności alkalicznej.
 System spękań z czarnymi produktami reakcji dedolomityzacji
 (minerały ilasto-krzemionkowe, brucyt) w obrębie ziarn kalcytu wtórnego (c). 1 polar (Góralczyk 2000)



Phot. 3 (SEM). Sample of Bielawy aggregate /B-III-5/ after the reactivity test.
 Cracked shell of crystalized thermonatrite.
 Spheres of higher crystallization levels can be noticed on the edges of the cracks (Góralczyk 2000)

Fot. 3 (SEM). Próbką kruszywa Bielawy /B-III-5/ po badaniu reaktywności.
 Spękana skorupa krystalicznego termonatrytu.
 Na krawędziach szczelin widoczne strefy o wyższym stopniu krystalizacji (Góralczyk 2000)



Phot. 4 (SEM). Sample of the Bielawy aggregate /B-II-5/ after the reactivity tests.
 Commonly present fan-shaped secondary calcite (Góralczyk 2000)

Fot. 4 (SEM). Próbką kruszywa Bielawy /B-II-5/ po badaniu reaktywności.
 Pospolicie występujący wachlarzykowaty wtórny kalcyt (Góralczyk 2000)

4. Analysis and discussion

Many authors studying the process of reactivity believe that alkali-carbonate reactions of aggregates (known as the dedolomitization) occur in all dolomite rocks (Hadley 1961, 1964). It is also strongly believed that the alkali-carbonate reactions (dedolomitization) have no influence on the size of expansion which, according to the authors, occurs due to interaction between the alkaline solutions and clay minerals. This reaction causes their dissolution and the formation of siliceous gel expanding similarly to clay minerals under the influence of water (Grattan-Bellew, Gilliot 1987; Sommer, Nixon, Sims 2005).

Looking at the results of the study on the alkaline reactivity of carbonate aggregates and their mineral and textural composition before and after reacting with alkalis, the following can be concluded: in the aggregates described as reactive after testing them with the ASTM 1260 – 94 method and “mortar-bar” method the alkaline reactions (dedolomitization) do occur. The reactions were detected by the products of the reaction (secondary calcite replacing dolomite, brucite and thermonatrite). At the same time, rocks which have undergone reactions changed their texture – loosened with cracks, often filled with the dedolomitization products.

The above mentioned processes that are the follow-ups of alkaline reactions were not found in the remaining samples. The remaining samples also did not show any reactive expansion. It can be therefore agreed that alkali-carbonate rock reactions cause dolomite disintegration with end products being primarily dolomite rocks with mineral composition containing amorphous silica, clay minerals and specific, reactive texture. The existing studies (Góralczyk 1993a, 1993b, 1994, 2000) define the quality characteristics of dolomite rocks that undergo alkaline reaction as follows:

- Mineral composition
 1. Dolomite content min. 23%
 2. Calcite content min. 48%
 3. Amorphous silica in a form of an opal or chalcedony content min. 5%
 4. Dry clay minerals content (kaolinite, illite, smectite) min. 4%
 5. Units insoluble in HCl content min. 4–5%
- Textural characteristics
 1. Size of the dolomite grains min. 0.05–0.13 mm
 2. Size of the calcite grains min. 0.005 mm
 3. Pores' diameter <0.005 mm
 4. Pores closed and isolated
 5. High density
 6. Texture description: solid and dense fine-crystalline rock, structured from calcite fine grains which surround the cluster of bigger dolomite grains in pores and inter-granular cracks. Clusters of clay minerals and amorphous silica in the form of opal and chalcedony are also present. The texture is genetically connected to secondary dolomites.

Content of dolomite and calcite (which are different to the one given above) do not influence the reactivity of the rock in a significant way. Fulfilling the remaining mineralogical and textural criteria is sufficient for the alkaline reactions to occur.

The current theory stating that all dolomite rocks are prone to alkaline reactions is therefore highly questionable.

The detailed mineralogical tests have proven that the reactive composition is related to the rock's secondary dolomite genesis. Rocks from the Bielawy deposit are secondary dolomitized. Creation of clay admixtures ("dry") and amorphous silica in the sedimentation period is the consequence of its genesis. It can therefore be concluded, with very high probability, that it is not the content of dolomites in rocks themselves but its genesis as a secondary dolomite and the mineralogical-textural consequences (admixture of amorphous and clay minerals) which are the main factors influencing the potential reactivity of aggregates in concrete.

Their mineralogical composition, especially the presence of clay-silica admixture, is the reason for which it is only the secondary dolomites that react with alkalis. The admixture plays the role of catalysts in dolomitization reactions, regulating the pH solution in which alkalis dissolve. Due to those minerals pH is alkaline and higher than 12.

The catalytic abilities of clay-silica admixtures are caused by its specific, absorptive properties. As a result of the attachment of Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions, the OH^- ions are most probably released, regulating the solution's pH and being able to react with dolomite crystals causing their disintegration (Grattan-Bellew, Gillott 1987).

Expansion occurred only in those samples where the alkaline reaction had been detected (Bielawy). The values of linear change for those samples are high (Fig. 1 and 2, Table 3). Simultaneously the mineralogical studies proved that the alkaline reactions occurred together with transformation phase, replacing dolomite with calcite, forming end products (brucite, thermonatrite) as well as hydrated aluminosilicate. Expansion appeared due to the textural changes resulting from alkaline reactions.

It has to be stressed that alkali-carbonate reactions of aggregates that occur in reactive dolomite rocks are the first step of the reactivity process, which later appears in a form of harmful expansive changes of aggregates in concrete. The mechanism of this process is as follows.

A very specific texture and mineralogical content of the reactive aggregate are the reasons for which the alkaline solutions (solution NaOH) are having difficulty penetrating (without constraint) far into the rock. Instead, they directly attack the dolomite grains connected to the solution or indirectly through diffusion by rich isolated dolomite grains. Depending on the distribution of mineral grains, solutions migrate inwards through the rock by:

- A) Reacting with dolomite that has been in contact with alkalis such as in formula 1.1. and consequently loosening the rocks' texture.
- B) Reacting with fine-crystalline calcite with results same as above.
- C) Contact with clay minerals and their removal and consequently purging the pores and cracks.

D) Diffusion of ions Na^+ and OH^- resulting from the difference in concentration outside and inside the pores in the rock.

As a result of the dedolomitization reaction dolomite decomposes and is replaced entirely or partially by fine-crystalline secondary calcite (formula 1.2). It is usually covered with a nontransparent “film” in a form of an amorphous substance, often cracked as a result of occurring dedolomitization ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$). Photo 3 illustrates the formation of thermonatrite’s structure. Brucite, due to its poor solubility, forms very quickly as one of the first products in close proximity to the decomposing dolomite.

Many products are formed as a result of the dedolomitization reaction. They usually adopt the form of an amorphous substance of a dark brown colour, difficult to identify using the microscopic method.

They concentrate in a form of reactive rims around the decomposing dolomite grains, secondary calcite and in concrete on the verge between aggregate grains and cement grout.

Dark products can be defined as silica gel enriched with calcium, iron, sodium, aluminium and magnesium. The silica gel has absorbing properties connecting the ions which can be found in pores’ solutions (Mg^{2+} , Na^+ , Ca^{2+} , AlO_2^+) as well as iron, forming hydrated silicas from those elements. This substance is one of the expansive factors. It is noticeable in the results of a test conducted with X-ray EDS probe (Fig. 5).

Reactive rims in samples from Bielawy usually consist of two spheres, sometimes of three spheres, but only rarely due to a low recognition ability:

- Sphere I with precipitated amorphous brucite.
- Sphere II with fine secondary calcite.
- Sphere III with precipitated silica (gel) of calcium, sodium and clay.

The formation, in an accordance to the dedolomitization reaction, of products described above is not the end of the phase transformation in samples from Bielawy. The secondary calcite, appearing in big quantities undergoes repeated dedolomitization as a result of the influence of ions Mg^{2+} that can be found in pores’ solutions. They originate from brucite created during the dedolomitization reaction. Brucite is dissolved as a result of its reaction with silica, becoming a solution and before the precipitation of silica gel ($(\text{Mg}) \text{SiO}_2 \cdot \text{H}_2\text{O}$) it can enrich secondary calcite with magnesium.

The process is fostered by high alkalinity ($\text{pH} > 12$) of the solutions that occur in pores (Hadley 1961). The discussed observations make it possible to conclude that the mechanisms and process of expansion in reactive carbonate rocks are multistage and complex processes. There is no doubt that the major role in forming pressure is played by the clay minerals and a cryptocrystalline quartz, as well as osmotic and crystallization pressure, all having a significant impact on expansion progress. The effects of this process had been widely noticed while conducting test (Phot. 2, 3).

Osmotic pressure is created around the dolomite grains in the limited inter-granular space formed by the fine calcite grains as a result of an increase in concentration of dissolved reaction’s end products. The membrane functions are most probably fulfilled by a fine brucite sediment precipitated in the first phase of the dedolomitization reaction.

The primary part of the products of the reaction dissolved in the pores' solution is not capable of infiltrating the brucite sediment, especially silicate rocks due to the size of their ions. However ions OH^- and Na^+ which are smaller in size can migrate easily. On the boundary of these two solutions the osmotic pressure is formed. It seems that its impact is long-term but the value is not high, which is the reason for its limited impact.

The changed texture of the rocks' samples, the placement and the formation of the reaction's products make it possible to conclude that the pressure, caused by the expansion and crystallization of new mineral phases, reaches higher values in the reactive samples.

Pressure resulting from expansion occurs in clay minerals and crypto-crystallized silica, and then absorbent silica gel. Those minerals that are present in cracks of small inter-granular spaces or rock pores expand under the influence of the solutions and then exert pressure on the walls.

It is therefore correct to believe that secondary dolomites which contain admixtures of clay minerals ("dry") and amorphous silica are potentially reactive rocks that can react with alkalis and cause damaging expansion in concrete.

5. Summary and conclusion

Studies of alkali-carbonate reaction of aggregates from the domestic deposits turned out to be of a high utility value and effective in identifying the discussed processes. On the basis of the results general characteristics of aggregates from carbonate rocks; their mineral composition, admixtures and texture, have been defined and described. Discussed in the paper petrological-mineral description of the reactive carbonate aggregates can also be used as a method of determining reactivity of a raw material in a deposit and evaluating its usability in concrete.

The conducted tests point out that both occurrence and size of expansion (linear changes) depend on the degree to which the dolomite had disintegrated as well as on the number of products formed through dedolomitization reactions (secondary calcite, brucite, thermonatrite). Alkaline reactions occur only in limited groups of dolomites, and in every case they result in damaging expansion.

It could appear that the reactivity of carbonate rocks can be a consequence of its genesis. The epigenetic dolomites with a specific texture and mineral composition, which contain secondary dolomite formed as a result of calcite dolomitization, are the most reactive and expansive.

It is caused by the clay-silica admixtures influence on alkali-carbonate reactions, regulating the pH value of solutions by which the alkali reactions occur. It is a practical indicator of a high value, able to become (already on the stage of providing documentation of deposits) an introductory, simple and cheap method of recognizing carbonated rock material in order to define its utility.

The expansion symptoms only appeared in those carbonate rocks in which mineral and textural changes occurred as a result of a dedolomitization reaction. Clay minerals and amorphous silica are connected to the sedimentation period, and their origin is significant in predicting their behavior in expansion and their ability to cause pressure in a rock.

It appears that the role that dolomite plays in reactive rocks is limited. It is not directly involved in generating expansion, it only takes part in alkaline reactions. However the texture of the rock has a significant impact on evoking pressure in a rock.

It can be concluded, with very high probability, that the process of alkaline-carbonate reactions in aggregates does not end with a complete disintegration of dolomite, but it keeps on progressing as dolomitization. Those reactions are therefore based on interchangeable dedolomitization and dolomitization of secondary calcite formed by dolomite's disintegration.

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REAKTYWNOŚĆ ALKALICZNA KRUSZYW WĘGLANOWYCH

Słowa kluczowe

Reaktywność alkalia-węglany, istota reakcji, wymagania, metody badań

Streszczenie

Kruszywa ze skał węglanowych stosowane są powszechnie w budownictwie między innymi do produkcji betonów. Niektóre z nich, zawierające w swym składzie mineralnym obok dolomitu domieszki minerałów ilastych i bezpostaciowej krzemionki, mogą reagować z alkalią powodując szkodliwą ekspansję w betonach. W artykule opisano istotę i mechanizmy tego zjawiska oraz zaproponowano efektywne metody oceny przydatności polskich kruszyw ze skał węglanowych do produkcji betonów. Podano kryteria jakościowe oceny reaktywności. Ustalono, że reakcje alkaliczne i ekspansja to dwa oddzielne zjawiska, ale genetycznie powiązane ze sobą. Ekspansji podlegają tylko te kruszywa, w których wystąpiły reakcje spowodowane występowaniem domieszek ilasto-krzemionkowych. Skład mineralny kruszyw ekspansywnych oraz ich tekstura wskazują, że szczególnie reaktywne są dolomity epigenetyczne o charakterystycznej teksturze.

Przemiany fazowe nie kończą się z chwilą całkowitego rozpadu dolomitu, lecz mają charakter cykliczny. Składają się one z następujących po sobie na przemian reakcji dedolomityzacji i dolomityzacji wtórnego kalcytu powstałego z rozpadu dolomitu. Wtórny kalcyt może ulegać oddziaływaniu jonów Mg^{+2} znajdujących się w roztworach porowych i tworzyć wtórny dolomit. Jony Mg^{+2} pochodzą z powstającego w procesie dedolomityzacji brucytu $[Mg(OH)_2]$, który w wyniku reakcji z krzemionką (SiO_2) może się rozpuszczać i wzbogacać wtórny kalcyt w magnez. Tak więc reakcje zachodzące w reaktywnych kruszywach węglanowych i betonach z nich wykonanych są procesami ciągłymi polegającymi na kolejnych przemianach dolomitu w kalcyt i odwrotnie, a także reakcją pomiędzy produktami dedolomityzacji (brucyt, krzemionka) i produktami dostarczonymi z zewnątrz (woda, alkalia). Opisane reakcje dedolomityzacji są etapem umożliwiającym tworzenie się zjawiska ekspansji w wyniku powstawania w porach międzyziarnowych ciśnienia jako efekt pęcznienia suchych minerałów ilastych pod wpływem roztworów wodnych.

Rozluźnienie struktury kruszywa jako efekt reakcji dedolomityzacji ułatwia migrację roztworów wodnych w głąb ziaren kruszywa i ich kontakt z minerałami ilastymi.

ALKALI – CARBONATE REACTION OF AGGREGATES

Key words

Alkali-carbonate reaction of aggregates, the essence of the reaction, requirements, methodology

Abstract

In the construction industry carbonate aggregates are commonly used in processes such as concrete production. Aggregates which contain (in their mineral composition) dolomite and an admixture of clay minerals and amorphous silica, can react with alkalis. These reactions can lead to a destructive expansion in concrete. This article explains the mechanisms and the essence of this phenomenon. What is more, some effective and fast methods of the estimation and evaluation of Polish aggregates consisting of carbonate rocks suggests effective methods to determine the usefulness of Polish carbonate aggregates in concrete production are discussed in the paper. Underneath the quality criteria to determine the reactivity of the aggregates will be given. It has been agreed that alkaline reaction and expansion are two separate phenomena related to each other genetically. The aggregates in which reactions caused by clay-siliceous admixtures occur are subjected to expansion. Mineral composition of expansive aggregates as well as their texture indicate that epigenetic dolomites with a distinctive texture are the most reactive.

The phase transformations do not end with a complete disintegration of dolomite. They have a cyclical character. They consist of interchangeable reactions of dedolomitization and dolomitization of secondary calcite formed as a result of dolomite's disintegration. The secondary calcite can be effected by Mg^{+2} ions from pores' solutions and it can form a secondary dolomite. The Mg^{2+} ions originate from brucite $[Mg(OH)_2]$, created in dolomitization process. As a consequence of its reaction with silica, brucite can dissolve and enrich secondary calcite with magnesium. Therefore the reactions which take place in reactive carbonate aggregates and concrete that is made of it are in fact ongoing processes which consist of dolomite's changes into calcite and vice versa. They are reactions between dedolomitization products (brucite, silica) and products from outside (water, alkalis). The described dedolomitization reactions are a phase of the process that enables expansion due to formation of pressure in inter-granular cracks, with pressure being a result of dry clay-minerals' expansion under the influence of water solutions.

Loosening of the aggregate's structure as an effect of dedolomitization reaction makes it easier for water solutions to migrate far into the aggregate's grains followed by their contact with clay minerals.