

dr Wiktor Jasiński^{1*)}

ORCID: 0000-0001-6612-4207

dr inż. Andrzej Duszyński¹⁾

ORCID: 0000-0002-8842-5630

mgr inż. Aneta Pryga-Szulc¹⁾

ORCID: 0000-0003-4233-3017

dr Wojciech Bartz²⁾

ORCID: 0000-0002-7267-2776

Assessment of selected limestone aggregates for potential alkaline reactivity in concrete

Ocena wybranych kruszyw wapiennych pod kątem wystąpienia potencjalnej reaktywności alkalicznej w betonie

DOI: 10.15199/33.2023.12.08

Abstract. The article presents the results of research work of potential alkaline reactivity of limestone aggregates. Potential alkaline reactivity tests were performed for the alkali-carbonate reaction (ACR) according to GDDKiA Procedure No. PB/2/18 (with permitted modifications for carbonate aggregates). However, in petrographic tests according to the guidelines contained in GDDKiA Procedure No. PB/3/18, attempts were made to include the possibility of two types of alkaline reactions, alkali-carbonates (ACR) and alkali-silica (ASR). The tests were carried out for three selected limestone aggregates in order to assess the possibility of their use in concrete. Based on the positive test results, the possibility of using these aggregates for concrete was confirmed.

Keywords: limestone aggregate; alkaline reactivity; petrography.

Streszczenie. W artykule zaprezentowano wyniki pracy badawczej dotyczącej zjawiska potencjalnej reaktywności alkalicznej kruszyw wapiennych. Badania wykonano pod kątem reakcji alkalia-węglany (ACR) wg Procedury GDDKiA nr PB/2/18 (z dopuszczoną modyfikacją w przypadku kruszyw węglanowych). Natomiast w badaniach petrograficznych wg wytycznych zawartych w Procedurze GDDKiA nr PB/3/18 starano się przeanalizować możliwość wystąpienia dwóch rodzajów reakcji alkalicznej, tj. alkalia-węglany (ACR) i alkalia-krzemionka (ASR). Badano trzy wybrane kruszywa wapienne w celu oceny możliwości ich stosowania do betonu. Na podstawie uzyskanych pozytywnych wyników badań potwierdzono możliwość stosowania tych kruszyw do betonów.

Słowa kluczowe: kruszywo wapienne; reaktywność alkaliczna; petrografia.

Owing to their favorable physico-mechanical properties and durability, carbonate aggregate (including limestone) is used in the production of concretes whose functional properties do not yield to concretes made from other aggregates [1]. Due to the potential contamination of the aggregate with clay minerals, various forms of silica, and a certain degree of dolomitization, they are exposed to unfavourable alkali-silica (ASR) and alkali-carbonate reactions (ACR) [1]. These processes, referred to as alkali-aggregate reactivity (AAR) processes, occur between potentially reactive minerals (including chalcedony, opal, tridymite, microcrystalline quartz, quartz in a state of „highly strained quartz”) and alkalis present in the cementitious mixtures. They are dangerous due to,

among others, slow and prolonged deterioration of concrete structures [2, 3]. Tests on the alkali reactivity regarding the occurrence of potential alkali-carbonate reaction (ACR) have been conducted, while petrographic examination has analysed the possibility of occurrence of both types of reactions: alkali-carbonate reactivity (ACR) and alkali-silica reactivity (ASR).

Methods for the examination of the alkali reactivity of aggregates

Currently, methods for the examination of the alkali reactivity of aggregates in Poland are mostly based on ASTM standards and RILEM guidelines included in the Research Procedures of the *General Directorate for National Roads and Motorways* (Generalna Dyrekcja Dróg Krajowych i Autostrad, (GDDKiA):

- PB/1/18 [4] „Procedure for the examination of aggregate reactivity by the accelerated method in a 1 M NaOH solution at 80°C.” The method involves

producing three concrete beams with dimensions of 25 x 25 x 250 mm and storing them in a 1 mol NaOH solution at a temperature of 80°C for 14 days. The average length increase of the samples is then calculated, and the aggregate is classified into the appropriate category R0 to R3. This method is exclusive for the alkali-silica reaction;

- PB/2/18 [5] „Procedure for the examination of aggregate reactivity at 38°C according to ASTM C1293/RILEM-AR-3.” The method involves producing three concrete beams with dimensions of 75 x 75 x 250 mm and storing them in a chamber at a temperature of 38 ± 2°C for 365 days. The evaluation of aggregate reactivity is based on the average length change of the samples, and the aggregate is assigned the category R0 to R3. This procedure has been modified compared to the original ASTM C 1293-20a method [6] and allows for the examination of the susceptibility of carbonate aggregates to alkali-carbonate reaction. PB/2/18 specifies that a change in the

¹⁾ Instytut Badawczy Dróg i Mostów – Filia Wrocław

²⁾ Uniwersytet Wrocławski, Instytut Nauk Geologicznych

^{*)} Correspondence address: w.jasinski@ibdim.edu.pl

length of the carbonate aggregate sample by at least 0.03% indicates susceptibility to alkali-carbonate reaction.

The diagnosis of the susceptibility of aggregates to alkali reactivity also includes a petrographic description (macroscopic and microscopic) which includes e.g., identification of rocks and potentially reactive constituents, as well as recognition of alkali-silica or alkali-carbonate reaction products. In Poland, the method according to PN-EN 932-3 [7] is currently used for petrographic analyses of aggregates. Additionally, GDDKiA has introduced an examination procedure outlined in the „Recommendations for Petrographic Analysis of Aggregates according to the Examination Procedure GDDKiA PB/3/18 [8],” which aims at determining potential occurrence of alkali-carbonate reactivity (ACR), among others [3].

Examination Subject, Scope, and Purpose

The subject of the examination was the petrographic analysis of limestone aggregates, representing the initial stage in assessing their suitability for use in transportation construction. The susceptibility of limestone aggregates to reaction with alkalis present in concrete (ACR) was evaluated.

The examination scope included the following:

- selection of limestone aggregates for petrographic analysis;
- macroscopic petrographic examination of limestone aggregates;
- microscopic petrographic examination of thin sections of limestone aggregates;
- determination of the phase composition of limestone aggregates using X-ray diffraction (XRD);
- thermal analysis of limestone aggregates;
- determination of chemical composition of limestone aggregates;
- petrographic description regarding the occurrence of alkali reactivity (AAR – ACR) based on thin sections derived from concrete beams.

For the examination according to the GDDKiA Examination Procedure No. PB/2/18 [5] and PB/3/18 [8], three types of limestone aggregates from different deposits in Poland were selected for the analysis and labelled as A, B, and C.

Petrographic examination methods

All the examined samples of limestone aggregate underwent macroscopic analysis according to PN-EN 932-3:2022 [7]. Based on this, representative samples were selected for further microscopic studies, X-ray diffraction analysis, thermal analysis, and chemical composition determination. Microscopic examinations of thin sections in reflected and transmitted light from beams after alkali reactivity tests were also conducted following the GDDKiA Examination Procedure No. PB/2/18 [5].

For the selected representative sample of limestone aggregate, microscopic preparations (thin sections for transmitted light) were made at the grinding facility of the Institute of Geological Sciences, University of Wrocław. The examinations were carried out using a Leica DM 750 P polarizing microscope.

To obtain an accurate characterization of the phase composition of the investigated limestone aggregate, powder X-ray diffraction (XRD) analysis was performed using a Bruker D8 Advanced diffractometer operating in Bragg – Brentano geometry at the Institute of Geological Sciences, University of Wrocław.

In order to determine the mineralogical composition of limestone aggregates, a thermal analysis was conducted using a Perkin Elmer STA 6000 thermal analyser at the Institute of Geological Sciences, University of Wrocław. The chemical composition of carbonate aggregates was determined using X-ray fluorescence (XRF) analysis in the Soil Science Laboratory of the Department of Physical Geography, University of Wrocław.

Thin sections for microscopic examinations in reflected and transmitted light were prepared from selected samples from concrete beams after alkali reactivity tests following the GDDKiA Examination Procedure No. PB/2/18 [5]. The examinations of thin sections in reflected and transmitted light were carried out using a Leica DM 750 P polarizing microscope.

Additionally, a petrographic description analysis regarding the potential occurrence of alkali reactivity (AAR – ACR) was conducted.

The Results (Report)

The results of microscopic petrographic description on thin sections for reflected and transmitted light according to ASTM C295/RILEMAAR-1.1 [9, 10] are presented in Table 1. Based on the determination of the phase composition (XRD) in samples A, B, C, the presence of reflections from a single mineral phase was observed: calcite (CaCO_3), with 2 θ values ranged from 0.105 to 0.149. An exemplary X-ray diffraction (XRD) phase diagram of sample A is presented in Figure 1.

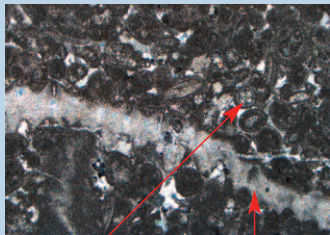
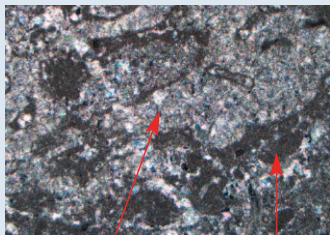
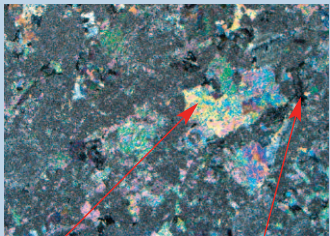
As a result of thermal analysis, the amount of CaCO_3 calculated based on the mass loss of sample A caused by the thermal dissociation of rhombohedral carbonates is approximately 97% by weight, for sample B – 98% by weight, and for sample C – 98.5% by weight. The thermogram illustrating the thermal analysis curve of sample A is shown in Figure 2.

The results of the determination of the percentage composition of chemical compounds in samples A, B, C subjected to geochemical analysis are presented in Table 2. Based on macroscopic analysis, microscopic analysis of thin sections in a polarizing microscope, determination of the phase composition using X-ray diffraction (XRD), and thermal analysis of carbonate aggregates labelled as A, B, C, it was concluded that they represent sedimentary carbonate rock, and their structure, texture, colour, and petrographic composition may indicate limestone.

In literature, guidelines, and standards, limestone is classified as a rock that may contain potentially reactive minerals in an amount that could influence the occurrence of the AAR process [3, 11]. According to the GDDKiA Examination Procedure PB/3/18 [8], if limestone with a CaCO_3 content > 95% does not show presence of potentially reactive components such as reactive forms of silica and clay minerals or specific texture, and if $\text{SiO}_2 < 3.0\%$, $\text{MgO} < 1.0\%$ (< 5% dolomite), and $\text{Al}_2\text{O}_3 < 1.2\%$, then the aggregate is not susceptible to ACR. Microscopic analysis conducted on thin sections of limestone aggregate A revealed the presen-

Table 1. Microscopic petrographic description based on ASTM C295/RILEM AAR-1.1 [9, 10]

Tabela 1. Mikroskopowy opis petrograficzny wg ASTM C295/RILEM AAR-1.1 [9, 10]

Sample	Microscopis description	Image under the microscope, transmitted light with the analyser, surface 4x/0.10
A	<p>xenomorphnic, occasionally hypautomorphic crystals of spar were observed, with sizes up to 0.8 mm, having a sinusoidal and amoeboidal shape. Additionally, there are grains of carbonate occurring between them, slightly turbid with a light brown tint, lacking distinct cleavage or twinning, forming micrite. Some spar crystals exhibit rhombohedral cleavage and polysynthetic twinning. The following features are visible:</p> <ul style="list-style-type: none"> – circular structures, likely peloids or ooids; – biogenic structures formed from organic substance; – vein structures, with small thickness, filled with microcrystalline carbonates, intersecting both spar and micrite; – xenomorphnic grains of silica minerals (likely chalcedony, microcrystalline quartz), with sizes up to 0.3 mm, and hypautomorphic grains of muscovite. Grains of silica minerals and muscovite occur as inclusions shaped like spar or between them; – non-transparent minerals, with sizes up to 0.1 mm, forming inclusions in the main minerals or occurring in the interstices between them. – stylolites (rusty-gold veins) formed due to the dissolution of clay minerals and minerals containing iron compounds. They traverse both grains and carbonate crystals, filling microcracks and interstices 	 <p>pelloidy/ooidy oraz struktury biologiczne struktura żyłowa wypełniona mikrokrystalicznym sparytem</p>
B	<p>visible are xenomorphnic, occasionally hypautomorphic crystals of spar with a simple, jagged, sinusoidal, and amoeboidal contact, sized up to 0.3 mm. Grains of carbonates occurring between them form micrite, distinctly turbid, with a light brown tint, lacking good cleavage or polysynthetic twinning. Spar crystals, occasionally, exhibit polysynthetic twinning. Additionally, the following features were observed:</p> <ul style="list-style-type: none"> – circular structures, likely peloids or ooids, and biogenic structures formed from organic substances; – vein structures intersecting spar and micrite, with slight thickness, filled with microcrystalline carbonates 	 <p>sparyt węglanowy mikryt węglanowy</p>
C	<p>large rock fractures are visible, xenomorphnic, sporadically hypautomorphic crystals of spar, with sizes up to 0.6 mm, embedded in carbonate grains forming micrite. The microspar has a light brown to light gray tint, lacking cleavage or polysynthetic twinning. Additionally, the following features were observed:</p> <ul style="list-style-type: none"> – biogenic structures formed from organic substances; – vein structures with slight thickness, filled with microcrystalline carbonates and spar; – non-transparent minerals with sizes up to 0.1 mm, forming inclusions in the main minerals or occurring in the interstices between them. Some non-transparent minerals show signs of weathering 	 <p>sparyt węglanowy minerały nieprzezroczyste</p>

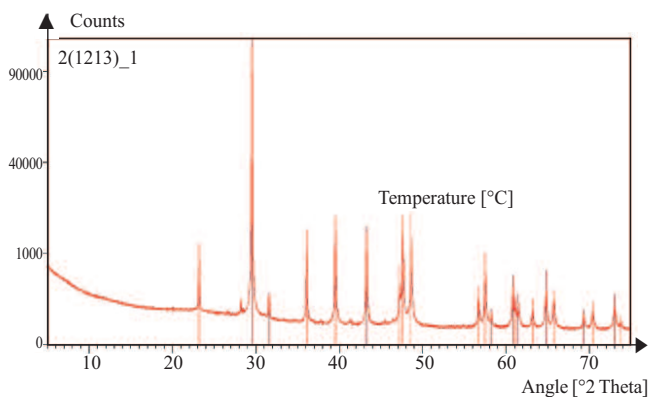


Fig. 1. Mineral phase diagram of the sample with symbol A
Rys. 1. Wykres fazy mineralnej próbki o symbolu A

ce of grains of silica minerals (likely chalcedony, microcrystalline quartz) belonging to potentially reactive minerals (according to AAR-1, Table A. 1.3 [11] and Table Z3.2. [3]), but due to their small quantity, reflections of these phases were not observed in the X-ray diffraction (XRD) analysis.

compounds, may indicate the presence of some amount of clay minerals. In the examined sample of aggregates B and C, no potentially reactive components such as forms of silica and clay minerals were identified, and the content of basic oxides was not exceeded. The results of the petrographic descrip-

Harmful ACR reaction is also favoured by the characteristic texture of the aggregate: the presence of rhombohedral dolomite crystals sized 20 to 50 µm, in a fine-grained matrix composed of microcrystalline calcite and clay minerals.

The presence of stylolite, likely formed through the dissolution of clay minerals and minerals containing iron

tion analysis regarding AAR are summarized in Table 3.

In light of the results of the petrographic description analysis for AAR, linear changes in concrete beams were investigated according to PB/2/18 [5], and microscopic examinations on thin sections in reflected and transmitted light of beam slices after alkali reactivity tests were conducted to determine the susceptibility of the examined limestone aggregate samples to ACR. **Based on the results of alkali reactivity tests according to the GDDKiA Examination Procedure PB/2/18 [5]**, it was determined that none of the selected limestone aggregates are reactive, as the linear changes did not exceed the permissible ones of 0.03% (Figure 3).

In the microscopic image on thin sections in reflected and transmitted light, no disturbing phenomena suggesting ongoing ACR processes were observed,

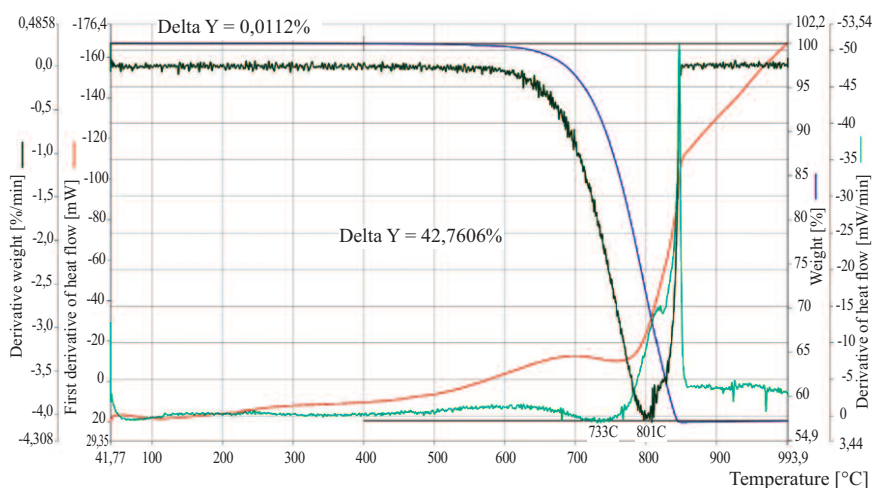


Fig. 2. Thermal analysis curves (thermogram) of sample with symbol A

Rys. 2. Krzywe analizy termicznej (termogram) próbki A

Table 2. Oxide contents

Tabela 2. Zawartość tlenków

Characteristic	Contribution [%]		
	sample A	sample B	sample C
SiO ₂	0,496	0,275	<0,1
CaO	54,880	55,120	55,234
MgO	0,551	0,394	0,404
Fe ₂ O ₃	0,063	0,069	0,082
Al ₂ O ₃	0,127	0,175	0,042
K ₂ O	0,014	0,012	< 0,01
TiO ₂	0,006	0,009	0,003
Na ₂ O	< 0,01	< 0,01	< 0,01
P ₂ O ₅	0,009	0,026	0,016
SO ₃	0,035	0,042	0,038
MnO ₂	0,011	0,017	0,010
Sum of the remaining:	43,770	43,850	44,150

including halos around grains filled with gel substance or micro-cracks filled with gel substance in the case of any of the tested samples.

Summary and conclusions

Petrographic examinations of sample A limestone aggregate revealed the presence of components and other characteristics that could influence the ACR process in concrete.

Table 3. Results of the analysis of the petrographic description in terms of AAR

Tabela 3. Wyniki analizy opisu petrograficznego pod kątem AAR

Tested sample	Content of chemical compounds/other features that may affect the AAR process in the tested samples					
	CaCO ₃	SiO ₂	MgO	Al ₂ O ₃	potentially reactive	other feature/internal structure
A	> 95%	0,496	0,551	0,127	probably: – chalcedony, – microcrystalline quartz	– presence of rhombohedral crystals of dolomite with a size ranging from 20 to 50 μm – presence of clay minerals and stylolites
B	> 95%	0,275	0,394	0,175	lack	lack
C	> 95%	< 0,1	0,404	0,042	lack	lack

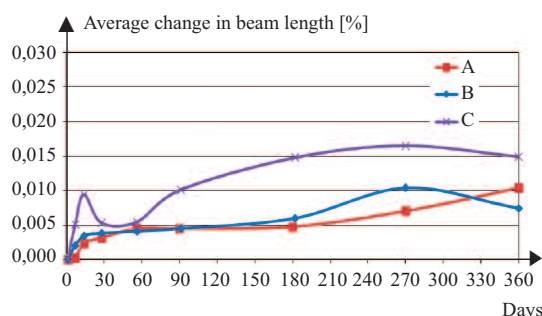


Fig. 3. Comparison of average linear changes of the examined beams with limestones

Rys. 3. Zestawienie średnich zmian liniowych badanych beleczek z kruszywami wapiennymi

In samples B and C, these components were not detected. Linear change studies in concrete beams confirmed the absence of ACR reactions for all the examined samples, as the average change in beam length did not exceed 0.03%, and no changes in the appearance of the external surface were noted. In the microscopic image on thin sections in transmitted light, no phenomena suggesting ongoing ACR processes were observed. The conducted investigations and analyses did not indicate the susceptibility of the examined limestone ag-

gregate samples to processes occurring between carbonates and alkalis present in concrete (ACR), thus, they confirmed their suitability for use in concrete.

Bibliography

[1] Łągosz A, Ulanowska D. Trwałość wybranych kruszyw wapiennych stosowanych do produkcji betonów w warunkach oddziaływania środowiska alkalicznego. Dni Betonu 2021, str. 1069 – 1085.

[2] Jasiński W, Duszyński A, Jórdeczka Ł, Pryga-Szulc A. Ocena kruszyw granitowych stosowanych do betonu pod względem wystąpienia potencjalnej reaktywności alkalicznej. Przegląd Geologiczny. 2020; 68 (10): 759 – 763.

[3] Garbacik A, Glinicki MA, Józwiak-Niedźwiedzka D, Adamski G, Gibas K. Wytyczne techniczne klasyfikacji kruszyw krajowych i zapobiegania reakcji alkalicznej w betonie stosowanym w nawierzchniach dróg i drogowych obiektach inżynierskich wraz z załącznikami, czerwiec 2019; Garbacik A., Glinicki M. A., Józwiak-Niedźwiedzka D., Adamski G., Bukowski L. aktualizacja kwiecień 2021.

[4] Procedura Badawcza GDDKiA nr PB/1/18 Instrukcja badania reaktywności kruszyw metodą przyspieszoną w 1 M roztworze NaOH w temperaturze 80°C. Załącznik nr 1. Wytyczne techniczne klasyfikacji kruszyw krajowych i zapobiegania reakcji alkalicznej w betonie stosowanym w nawierzchniach dróg i drogowych obiektach inżynierskich.

[5] Procedura Badawcza GDDKiA nr PB/2/18 Instrukcja badania reaktywności kruszyw w temperaturze 38°C wg ASTM C1293/RILEM AAR-3. Załącznik nr 2. Wytyczne techniczne klasyfikacji kruszyw krajowych i zapobiegania reakcji alkalicznej w betonie stosowanym w nawierzchniach dróg i drogowych obiektach inżynierskich.

[6] ASTM C 1293 Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction (Standardowa metoda badawcza do określania zmiany długości beleczek betonowych w wyniku reakcji alkalia-krzemionka).

[7] PN-EN 932-3:1999+A1:2004 Badania podstawowych właściwości kruszyw. Procedura i terminologia uściwionego opisu petrograficznego.

[8] Procedura Badawcza GDDKiA nr PB/3/18 Analiza petrograficzna kruszyw. Załącznik nr 3. Wytyczne techniczne klasyfikacji kruszyw krajowych i zapobiegania reakcji alkalicznej w betonie stosowanym w nawierzchniach dróg i drogowych obiektach inżynierskich.

[9] ASTM C 295-03 Standard Guide for Petrographic Examination of Aggregates for Concrete (Przewodnik do badań petrograficznych kruszyw do betonu).

[10] RILEM AAR-1.1 Detection of potential alkali-reactivity of aggregates – Petrographic method (Wykrywanie potencjalnej reaktywności alkalicznej kruszyw – metoda petrograficzna).

[11] RILEM Recommended Test Method AAR-1: Detection of potential alkali-reactivity of aggregates- Petrographic method, RILEM TC 191-ARP, Materials and Structures, Vol. 36, August-September 2003, pp 480-496.

Accepted for publications: 21.11.2023 r.