

INFLUENCE OF BARITE COMPOSITION ON POTENTIAL ALKALI AGGREGATE REACTION IN RADIATION-SHIELDING CONCRETE

Daria Józwiak-Niedźwiedzka¹, Karolina Gibas², Andrzej M. Brandt³, and Piotr Denis⁴

Institute of Fundamental Technological Research, Polish Academy of Sciences, Warsaw

¹Ph.D., (djozwiak@ippt.pan.pl), ²M.Sc., (kgibas@ippt.pan.pl), ³Prof., (abrandt@ippt.pan.pl),

⁴M.Sc., (pdenis@ippt.pan.pl)

Introduction

Concrete is used universally as a basic material for shields against ionizing radiation in various buildings related to nuclear power structures and for other applications of fission materials, e.g. for material testing, therapeutic treatment installations and radioactive materials deposits. In order to fulfil their structural functions, concrete containment walls should have sufficient durability; therefore the control of the ageing of concrete is necessary in all conditions of exploitation. Apart from climatic actions there are serious problems related to the influence of radiation on concrete microstructure and its properties during many years, [1], because there are several degradation mechanisms that could cause widespread ageing damage to the concrete walls e.g.: alkali–silica reactions (ASR); modification of micropores system due to heterogeneous thermal expansions; corrosion of reinforcing steel due to microcracking of cement matrix; sulphate attack and the others, [2]. The presence of these mechanisms is not easily detectable and they have potential to cause concrete cracking and strength loss.

The concrete usually used in nuclear safety-related plants is composed of Type II Portland cement, water, various supplementary cementitious materials, and admixtures for improving properties or performance of the concrete, and either normal-weight, heavyweight or special coarse and fine aggregate or even their combination. For those concrete structures in nuclear power plants that provide primary (biological) radiation shielding, heavyweight, or dense aggregate materials, such as barites, limonites, magnetites, ilmenites, etc., may be used to reduce the thickness of walls required for attenuation of radiation, [3]. Aggregate constitutes about 70% of concrete mass and cannot be treated as an unimportant filler because it participates at various processes due to ageing and ionizing radiation. Therefore, there is a considerable risk that

degradation mechanisms, namely alkali-aggregate reaction (AAR), may take place in concrete surrounding the pressure vessel of a nuclear reactor.

The reactive minerals in aggregate may be present in a small amount and their distribution may vary among aggregates. Damage can be caused by as little as 0.5% of defective aggregate. The magnitude of swelling decreases with the increase of aggregate porosity thanks to the ability of expanding gel that may be accommodated by porous aggregates without causing concrete expansion. Exposure to water is essential for swelling of the expansive alkali-silica gel. Therefore, most damage was observed in hydraulic structures or below grade portions of structures exposed to high water level. Elevated temperature in the range of 50-80°C appears in concrete walls around nuclear reactor and accelerates alkali-silica reactions (ASR), [2].

In the design of mix proportions an appropriate resistance against damage from elevated temperature should be ensured but barite aggregates cannot withstand high temperature because their thermal expansion is anisotropic and is different than in cement paste. Thermal expansion coefficient of barite concrete is twice as high as that of ordinary concrete. Therefore, barite concrete should not be exposed to temperature over 80°C (certain authors allow 100°C); limonite concrete may be accepted up to 200°C, [6].

As suggested by Morinaga [8] decrease of the resistance to nuclear radiation with increasing the content of SiO₂ in aggregate strongly indicates that the deterioration is due to the acceleration of AAR of concrete, or to alkali-silica reaction of aggregates in concrete by nuclear radiation, [7]. Ichikawa and Koizumi [7] concluded that distorted amorphous quartz generated on the surface of quartz by irradiation of a 200 keV Ar ion beam is at least 700 times and 2.5 times more reactive to alkali than crystalline and regular amorphous quartz, respectively. The high reactivity of the distorted amorphous quartz indicated that the degradation of concrete by ASR was possible to be induced by nuclear radiation even if the aggregates were inert to alkalis before the irradiation. Also Ichikawa and Kimura [4] have shown the results of ASR due to moderate doses of radiation of the order of 10⁶ rad and 1016 n/cm² when plagioclase-rich aggregate, such as andesite, was used in concrete, even if that concrete with aggregate was initially inert to ASR. Clifton [5] suggested also that the probability of structural damages due to ASR was very low in heavy reinforced concrete shields, but it is not impossible, [1].

According to the results of a report on ageing of reinforced concrete structures in nuclear power plants, [3], it has been stated that technical basis does not exist for quantitatively

estimation of the effects of some degradation mechanisms (e.g., AAR) on the service life of concrete structures. Concrete may continue to deteriorate as long as moisture is present. Crack repair methods will be ineffective because the AAR cannot be stopped. Therefore, it is necessary to select such composition of concrete for shields to avoid AAR cracks and loss of protections against radiation. Such requirement is particularly important for nuclear reactors and medical installations where ionizing radiation should be attenuated for safety requirements.

In the paper the barite aggregate has been analyzed as a potential source of ASR in heavy concrete. Special attention was paid to BaSO₄ and minor mineral components in aggregates and their influence on ASR development in tested mortars.

Materials and test methods

The influence of the kind of barite aggregate on specimen expansion and increase of length was studied. The research covered four kinds of barium aggregates, designated as B1, B2, B3 and B4, supplied from different sources and differing in content of BaSO₄, Fig. 1. ASTM C1260 Standard Test Method was used that allowed to detect the potential for deleterious alkali-silica reaction of aggregate in mortar bar exposed to NaOH solution in 80°C, [6],[7]. The tests were performed on mortar specimens; water-cementitious ratio was 0.47 and the cement to aggregate ratio 1:1.25. Standard ASTM C1260 does not specify the alkali content in cement; in ordinary Portland cement CEM I 42.5R that was used in the research Na₂O = 0.12% and K₂O = 0.78%.

The aggregate was crushed and sieved according to standard requirements, Table 1. Four mortar beams 25x25x285 mm were prepared for each barite aggregate (B1, ..., B4). After 24 hours in 23±2°C and RH ≥ 95%, the specimens were stored in 1N NaOH solution in climatic chamber in temperature 80±1°C and RH≥98% for next 14 days. The test was prolonged to 56 days in order to trigger the stronger influence of NaOH solution and temperature on the barite aggregates. The subsequent comparative readings of the specimens were performed first day, and then periodically, according to ASTM C1260. That test method permitted to detect the potential for deleterious alkali-silica reaction of aggregate in mortar bars during a relatively short period of time. If the expansion of the mortar beams after 14 days of testing is lower than 0.10%, the aggregate may be considered as resistant to alkali-aggregate reaction.

Table 1. Grading requirements of tested aggregates according to ASTM C1260

Sieve size [mm] retained on - passing	Mass [%]
2.36 – 4.75	10
1.18 – 2.36	25
0.6 – 1.18	25
0.3 – 0.6	25
0.15 – 0.3	15

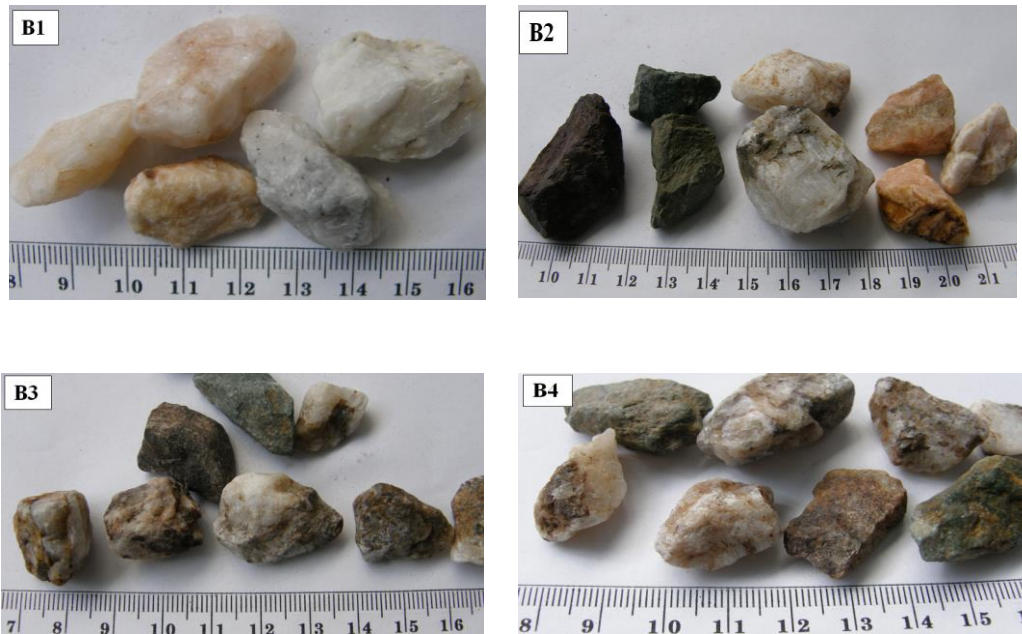


Fig. 1. Barite aggregates used in the research, cm

Aggregates were analyzed using wide angle X-ray scattering (WAXS) diffraction method before starting the test of the mortars expansion. The aggregates for the X-ray analysis were powdered and sieved through a 0.045 mm sieve. The Bruker D8 Discover diffractometer was used with a voltage ratio of 40kV and 40mA lamp current. Copper lamp was applied as an X-ray source. That technique was applied to mortars after 56 day of exposure to 1N NaOH.

Additionally, the fluorescent epoxy impregnated thin sections were prepared from aggregate grains before ASTM C1260 test and from mortars before and after 56 days of testing.

The contents of the main minerals in barite were tested and provided by aggregate suppliers and the results are presented in Table 2.

Table 2. Mineralogical phase composition of tested barite aggregates

Mineral composition, %	B1	B2	B3	B4
BaSO ₄	92	78.3	90	77.5
FeCO ₃	< 1%	< 1%	-	< 1%
CaF ₂	3	-	5	-
SiO ₂	3	2	3	3
others:				
CaMg[CO ₃] ₂	< 1%	< 1%	< 1%	< 1%
CaCO ₃				
Density, g/cm ³	4.2	4.18	4.05	4.15

Results and discussion

Diffraction patterns of barite aggregates are shown in Fig. 2. Not only barium sulphate is present in the samples, but also quartz (SiO₂), hawleyite (CdS), fluorite (CaF₂) and siderite (FeCO₃); this is indicated by characteristic reflections. In one aggregate only – B3 - the presence of pringleite, mineral from the borates cluster, is identified also.

In the rocks with barites also other minerals are often contained, these are: fluorite, quartz, carbonates and sulphides, Kilincarslan et al. [9]. In the tested aggregates B1 and B3 there were no carbonates and that observation indicates their origin from barite-fluorite formation. On the contrary, carbonates were found in the form of siderite in aggregates B2 and B4.

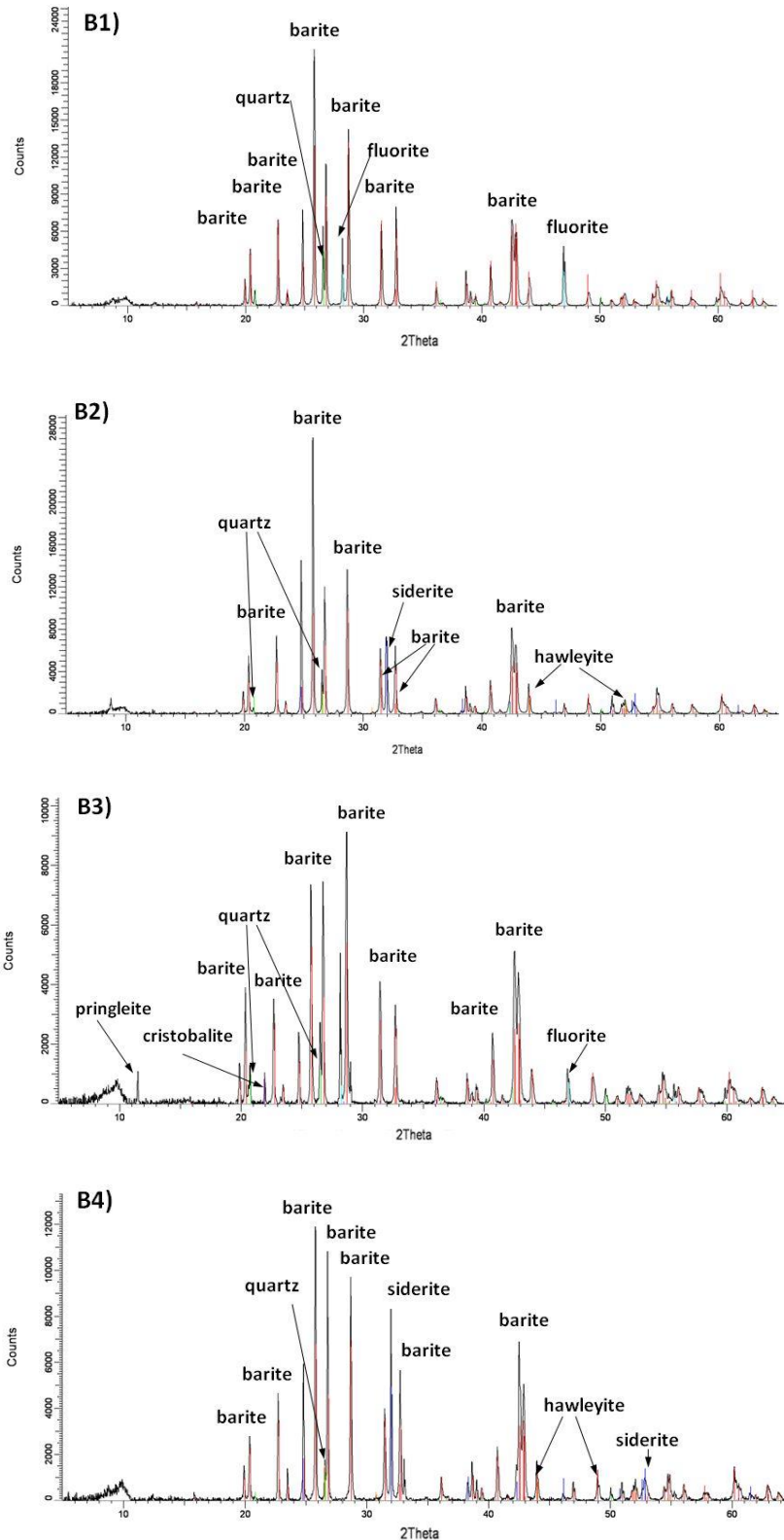


Fig. 2. Diffraction patterns of barite aggregates: a) B1, b) B2, c) B3 and d) B4

In aggregate B3 cristobalite was found, which is a reactive component, Fig. 2. Owsiak [10] and Kim [11] have found out that the aggregates with cristobalite were characterized by particularly high reactivity. After Farny and Kosmatka [12], even with as small amount as 1% cristobalite in the aggregate is at risk of ASR in the concrete. On the contrary, in no sample of tested barites the existence of neither anhydrite nor gypsum was found. Gypsum and other compounds of sulphur are rather frequently found in barite deposits, Lee et al. [13]. Sulphates may react in concrete with hydrated calcium carbonates creating ettringite and that is accompanied with expansion and cracking in the cement based matrix. Obtained diffraction patterns indicate that the mineral composition of barite aggregates is variable which should be considered before designing heavy concretes because of their required durability.

Results of expansion of the beams (average from three beams) as functions of storage times in solution of 1N NaOH are shown in Fig. 3. The beams were prepared with four different mortars with barite aggregates B1, B2, B3 and B4. Dotted red line indicates maximum admissible value of linear elongation for specimens with aggregates that do not show any reactivity after 14 days according to ASTM C1260. Expansion lower than 0.1% of initial value indicates non reactive aggregate. Elongation between 0.1 and 0.25% shows that the aggregate was characterized by low reactivity while elongation above 0.25 indicates very reactive aggregates, Owsiak [10].

ASTM C1260 test is concluded after 14 days on the beams immersed in 1N NaOH, but for better estimation of the barite aggregates with respect to their applicability and to analyze the ASR in mortars on thin sections the measurements were continued during 56 days. After 14 days of storage two kinds of barite showed rather rapid increase of elongation. Both mortars B1 and B3 contained fluorite and B3 cristobalite also; the beams made with these mortars showed elongations over 0.2% after 56 days. All tested mortar beams did not exceed the criterion of 0.1% for expansion measurement after 14 days of testing.

The results of measured expansion after 14 days prove that the barite aggregates are characterized by different reactivity in function of their origin, and consequently of their mineral composition. The worst results were obtained for aggregate B3 with cristobalite; mortars made with aggregate B4 that contained siderite showed the lowest expansion. The longer influence of the elevated temperature and alkali environment was needed to create ASR, that is why tests were prolonged up to 56 days, followed by further microstructure analysis.

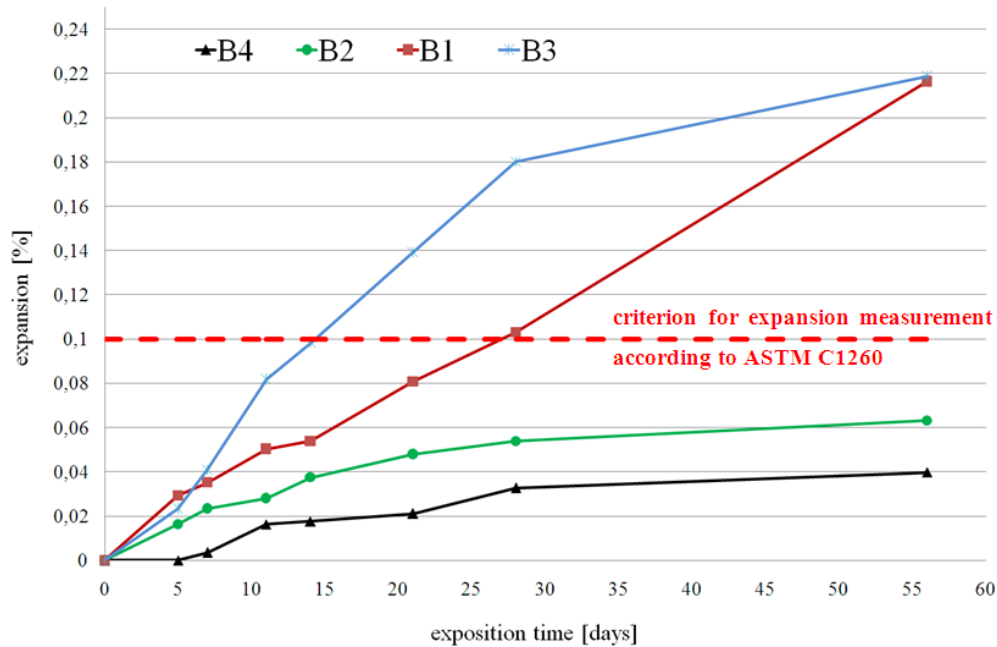


Fig. 3. Expansion of four mortar beams (B1, B2, B3 and B4) stored in 1N NaOH and temperature 80°C during 56 days

The analysis of the mortars after 56 days of storage in 1N NaOH and 80°C was performed on thin sections in polarized light. The results of the microscopic observations revealed that ASR occurred in all mortars, Fig. 4. The strongest influence of alkali-silica gel on the aggregate and matrix was visible in mortars with aggregate B1 and B3, which is in accordance with results from ASTM C1260 test method. In mortar B1 expansive gel has penetrated from fine aggregate into cement matrix and smaller aggregate grains were deteriorated also. The main reason of ASR occurrence in mortar B3 was coarse aggregate and in several larger grains alkali-silica gel was visible on their surface, Fig. 5. Also the characteristic reactions rim along the coarse aggregate grains outer periphery was noticeable. In mortars B2 and B4 minor traces of ASR have been found and only a few of fine grains have shown the signs of that reaction. In comparison to mortars with B1 and B3 aggregates, the size (Fig. 5, 6) and quantity of the alkali-silica gel in mortars with B2 and B4 aggregates were smaller. In all mortars the cracks were filled with secondary deposits known as expansive ASR products, but that process is better visible in B1 and B3 mortars.

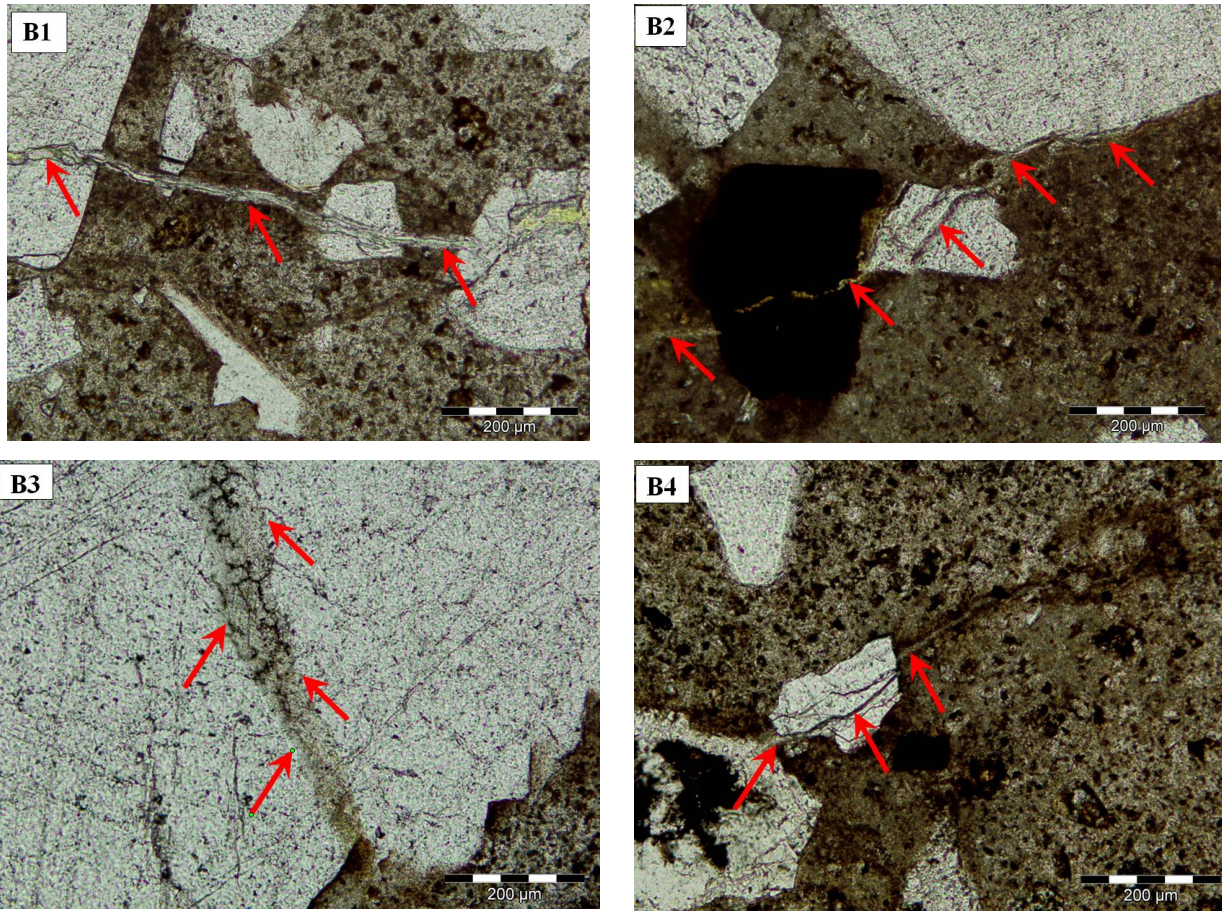


Fig. 4. Micrograph of mortars after 56 days of exposition in 1N NaOH and 80°C; thin section in polarized light, red arrows indicate the alkali-silica gel, mag.100x

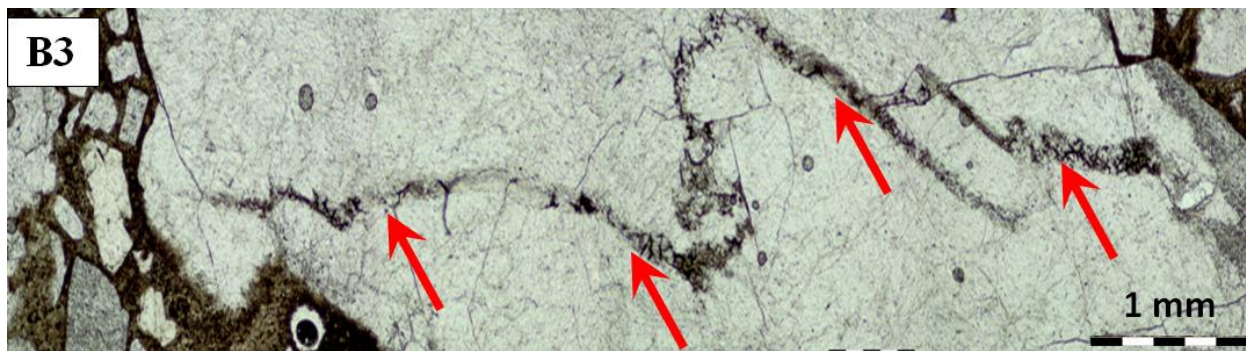


Fig. 5. Micrograph of mortars B3 after 56 days of exposition in 1N NaOH and 80°C; thin section in polarized light, red arrows indicate the alkali-silica gel, mag.40x

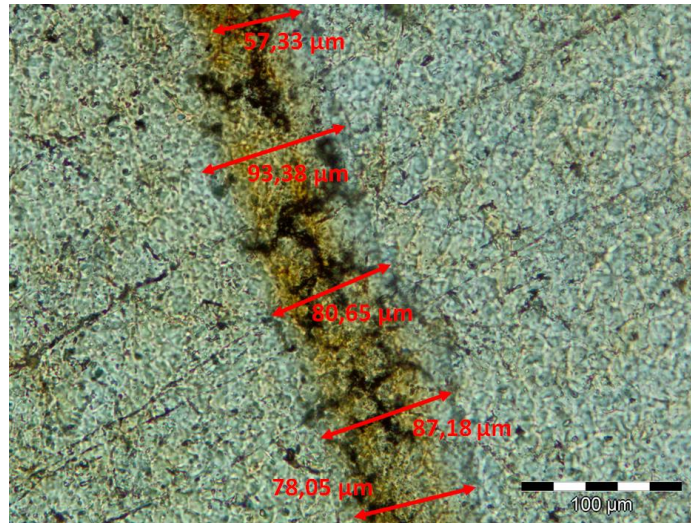


Fig. 6. Micrograph of mortars B3 after 56 days of exposition in 1N NaOH and 80°C; thin section in cross polarized light with gypsum plate, red arrows indicate width of a crack with ASR gel, mag.400x

Conclusions

The tests showed that mineral composition of four barite aggregates strongly influenced the induction of ASR in tested mortars. All mortars exhibited evidence of ASR but with different intensity. The worst result according to ASTM C1260 were found with B3 barite aggregate, which was characterised by the highest cristobalite content among all the tested barites.

The microstructural analysis on thin sections confirmed the expansion of grains in mortars. The most susceptible for ASR were aggregates B3 and B1. The reactive cristobalite was the source of ASR in coarse aggregate B3. Also fine grains in aggregate B1 were prone to destructive ASR. The results were cracks and microcracks that occurred within rimmed barite coarse aggregate grains, with cracks radiating out from the reacting grains into adjacent cement paste in mortars B1 and B3.

It was evident that silica-rich aggregate, especially its amorphous form of cristobalite, was prone to react with alkalis even as the aggregates were carefully selected to be apparently inert to ASR, but also the aggregates considered as safe were susceptible to NaOH solution and elevated temperature. It has been found that the type of aggregate plays an important role when the effectiveness of protection against X-ray and other radiation of cement mortars is expected.

Concrete surrounding the pressure vessel of a nuclear reactor as a shielding material receives the highest radiation dose among concrete structures in a nuclear power plant, [7], so the

temperature in concrete mass can arise up to 60-80°C. As far as the humidity will be maintained at the same low level <70% R.H. the risk of ASR seems to be small.

Because there is a strong risk that aggregates even carefully selected with respect to threat of ASR may stimulate such effects in favourable environmental condition, the binder – Portland cement – should be characterised with very low content of alkalis.

ACKNOWLEDGMENT

The results presented in the paper were obtained within the project “Durability and efficiency of concrete shields against ionizing radiation in nuclear power structures” (Project no PBSII/A2/15/2014), National Centre for Research and Development.

WAXS investigations were carried out with the use of CePT infrastructure financed by the European Union-the European Regional Development Fund within the Operational Programme “Innovative economy” for 2007-2013.

REFERENCES

- [1] Brandt A.M., Józwiak-Niedźwiedzka D., The influence of ionizing radiation on microstructure and properties of concrete shields – a review, *Cement Lime Concrete*, No 4, 216-237 (2013)
- [2] Shah V.N., Hookham C.J., Long-term aging of light water reactor concrete containments, *Nuclear Engineering and Design* 185, 51–81 (1998)
- [3] Naus D.J., Oland C.B., Ellingwood R., Report on aging of nuclear power plant reinforced concrete structures, NUREG/CR-6424, ORNL/TM-13148, pp. 300 (1996)
- [4] Ichikawa T., Kimura T., Effect of nuclear radiation on alkali-silica reaction of concrete. *J. of Nuclear Science and Technology*, 44, 10, 1281-1284 (2007)
- [5] Clifton R. J., Predicting the remaining service life of concrete. NISTIR-4712, s. 74,(1991)
- [6] Brandt, A.M., Application of concrete as a material for anti-radiation shielding – a review, *Cement Lime Concrete*, No 2, 115-132 (2013)
- [7] Ichikawa T., Koizumi H., Possibility of radiation-induced degradation of concrete by alkali-silica reaction of aggregates, *Journal of Nuclear Science and Technology*, Vol. 39, No. 8, p. 880–884 (2002)

- [8] Morinaga S., Preprint East Asia Alkali-Aggregate Reaction Seminar, Tottori, Japan, Nov. 23–25, 1997, p. 101 (1997)
- [9] Kilincarslan S., Akhurt I., Basyigit C., The effect of barite rate on some physical and mechanical properties of concrete, *Mat. Sc. Eng., A* 424, 83-86 (2006)
- [10] Owsiak Z., The alkali-silica reaction in concrete, *Ceramics, Polish Ceramic Bulletin*, Vol. 72, pp. 107 (2002)
- [11] Kim T., Alkali-silica reaction: Chemical mechanism, thermodynamic modelling, and effects of lithium ions, Ph.D. Thesis, Purdue University, pp. 230 (2013)
- [12] Farny J.A., Kosmatka S.H., Diagnosis and control of alkali-aggregate reactions in concrete, Portland Cement Association, IS413, pp. 22 (1997)
- [13] Lee S.Y., Daugherty A.M., Broton D.J., Assessing aggregates for radiation-shielding concrete, methods for petrographic examination of high-density and boron bearing aggregates, *Concr. Int.*, 35, 31-38 (2013)