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Mineral composition of heavy aggregates for nuclear shielding concrete in relation to alkali-silica reaction

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Abstract

The results of microscopic analysis on thin sections of aggregates intended for nuclear shielding concrete are presented. The petrographic analysis was performed on different barite, magnetite and hematite aggregates used as the high-density aggregate to absorb gamma radiation. Both optical microscopy and accelerated expansion tests were used to recognise the potential for alkali-reactivity of the aggregates. The mineral composition of the tested aggregates was analysed on thin sections in transmitted cross-polarized light and XRD tests were additionally performed. Expansion tests of mortar bars exposed to 1 N NaOH solution at the temperature of 80°C were also performed following ASTM C1260. The high-density aggregates contained ore deposits - metallic opaque phases providing the required shielding properties. These aggregates also contained various amounts of non-metallic phases, with both innocuous non-ore minerals and deleterious, potentially reactive materials. Barite aggregates contained siderite, fluorite and hawleyite in varying amounts, apart from the barium sulphate being the principal component. Moreover, particularly reactive cristobalite and muscovite were identified in barite aggregates from certain quarries. Tests according to ASTM C1260 performed on mortars showed the expansion above the accepted criterion for non-reactive aggregate and confirmed the threat due to the presence of cristobalite in barite aggregates.

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1. Introduction

No structural collapse related to alkali silica reaction (ASR) in concrete has been reported in the literature, however the cracks resulting from ASR expansion can provide direct paths for penetrating aggressive media. The impermeability of concrete in the reactor containment building is a safeguard against a release of radioactive materials (water, gases) into the atmosphere in a case of a cooling pipe failure. Therefore the design considerations of reactor containment and other safety-related buildings cover both operational and low-probability incidental loads, along with a detailed analysis of environmental and material factors influencing the long term performance of concrete structures. So the issue of potential ASR damage in concrete is of primary importance for safety-related structures in nuclear power plants. The damages to concrete may be more significant for an increased temperature and humidity of environment. The reactive minerals in aggregate may be present in small amounts and their distribution may vary in different portions of the aggregate. Damage can be caused by as small percentage as 0.5% of defective aggregates. The amount of reactive silica is an important factor governing the severity of ASR, which depends critically on the nature of the reactive aggregate. Highly reactive minerals like opal may cover as little as 2 % mass to cause deleterious expansion, while less reactive minerals such as greywackes require in excess of 20% to be dangerous, Oberholster [1].

Although the alkali reactivity of major types of aggregates used for concrete roads, bridges and dams has been studied thoroughly, Farny and Kosmatka [2], Fournier et al. [3], only few studies were devoted to such characterization of heavy aggregates used for concrete radiation shielding. Lee et al. [4] examined the methods for assessing aggregates for radiation shielding and stated that the aggregates should be relatively clean, free of deleterious materials, and chemically inert. An accurate identification and evaluation of presence of possible harmful materials is often the most critical part of petrographic examination. The common types of potentially deleterious materials in aggregates include mainly siliceous components of aggregate that are known to exhibit the potential for reaction with alkali hydroxides present in pore water of concrete. Since a prolonged exposure to nuclear reactor radiation may increase the risk of ASR damage in concrete, Pomaro et al. [5], Ichikawa et al. [6], Brandt et. al. [7] there is a need to resolve the issue of ASR potential of heavyweight aggregate.

The investigation of the mineral composition of different heavy aggregates is reported in this paper. The microscopic analysis in transmitted light on thin sections was used to identify the reactive components in heavy aggregates. Tests were focused on characterization of siliceous minerals in the aggregates, including the image analysis of quartz crystals size and distribution.

2. Materials and laboratory test methods

2.1. Materials

Three types of high-density aggregates were tested: a) barite, b) magnetite and c) hematite. Barite aggregate was imported from four different mines localized in Europe that were marked as B1 - Germany, B2 – Czech Republic, B3 - Poland and B4 – Czech Republic. Magnetite (M) was also collected from European mines (Sweden), and hematite (H) was from Morocco. In Fig. 1 a general view of tested aggregates is presented. Tables 1 and 2 present the mineral composition of aggregates. In two barite aggregates B1 and B3 the high content of BaSO₄ (barium sulfate) was discovered, i.e. more than 90%, while in barite aggregates B2 and B4 the BaSO₄ content only appr. 78% was found. According to the Standard PN-C-84088-06:1983 the content of BaSO₄ for special heavy concretes should amount to 75% at least. The Fe₂O₃ content in magnetite and hematite was above 85%.

Tested aggregates were characterised with following densities: barites 4-4.2 g/cm³, magnetites 4.8 g/cm³ and hematites 5.1 g/cm³. Such density makes them useful for heavyweight concrete, allowing for a designed high density of concretes, usually specified in shielding elements.



Fig. 1. Photographs of barite grains(a) B1 from Germany; (b) B2 from Czech Republic(c) B3 from Poland ; (d) B4 from Czech Republic, (e) magnetite from Sweden; (f) hematite from Morocco.

Table 1. Main components of barite aggregate after XRF method in %, supplier data.

Main mineral constituents	Barite B1	Barite B2	Barite B3	Barite B4
BaSO ₄	92	78.3	90	77.5
FeCO ₃	< 1%	< 1%	-	< 1%
CaF ₂	3	-	5	-
SiO ₂	3	2	3	3
density, g/cm ³	4.2	4.18	4.05	4.15

Table 2. Main components magnetite and hematite after XRF method, supplier data.

Main mineral constituents. %	Magnetite	Hematite
SiO ₂	3	11.5
Fe ₂ O ₃	90.8	85.08
Al ₂ O ₃	0.4	0.9
CaO	2.5	0.05
K ₂ O	0.2	0.4
Na ₂ O	0.3	0.02
density. g/cm ³	4.8	5.1

2.2. Testing methods

Thin sections

The fluorescent epoxy impregnated thin sections were prepared. Depending on the aggregate size, small grains were first impregnated and then cut into slices, while bigger grains were cut straightaway and then vacuum impregnated. The aggregate was grinded and polished to 20 μm thickness. Thin section analyses were carried on using the optical polarizing microscope Olympus BX51 connected to a digital camera. Thin sections were examined in plane polarized light (PPL), crossed polarized light (XPL), also with lambda plate, and in fluorescent light. The identification and analysis of minerals was performed in PPL and XPL, and the information about microstructure of aggregates or their eventual defects like microcracking or open porosity was collected in UV light.

X-ray diffractometry

The aggregates for analysis of the mineral composition using X-ray diffraction method 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 used as an X-ray source. The scan step size was 0.02 deg, collection time 1s and in the range 2θ CuK α from 5 to 65 deg.

ASTM C1260 expansion tests

The aggregate was crushed and sieved according to standard requirements. Four mortar bars 25x25x285 mm were prepared for each aggregate. After 24 hours in $23\pm 2^\circ\text{C}$ and $\text{RH} \geq 95\%$, the specimens were stored in 1N NaOH solution in a climatic chamber in temperature $80\pm 1^\circ\text{C}$ and $\text{RH} \geq 98\%$ for next 14 days. The subsequent comparative readings of the specimens were performed on the first day, and then periodically up to 14 days, 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 bars after 14 days of testing is lower than 0.10%, the aggregate may be considered as non-reactive.

3. Results and discussion

The characteristic view of barite aggregate is shown in Fig. 2. The thin section image of radial growths of barite B2 observed in cross polarized light shows "plumose" (like feathers) interference structure. Barite B2 consisted mostly of BaSO_4 crystals, and only a few of SiO_2 crystals were visible, which were too big (medium grained - more than 1 mm) to influence the appearance of ASR. The crystals of siderite were visible on thin sections also, but they need not be taken into consideration in relation to ASR. Similar observations were made for barite B4, and the siderite crystals are shown in Fig. 3. The siderite is characterised by brown colour on thin sections. The presented images on thin sections were observed with three different polarizer filters: plane polarized light (PPL), cross-polarized light (XPL), and cross-polarized light with lambda plate.



Fig. 2. Radial growths of barite B2 crystals, after XPL (scale bar = 2 mm).

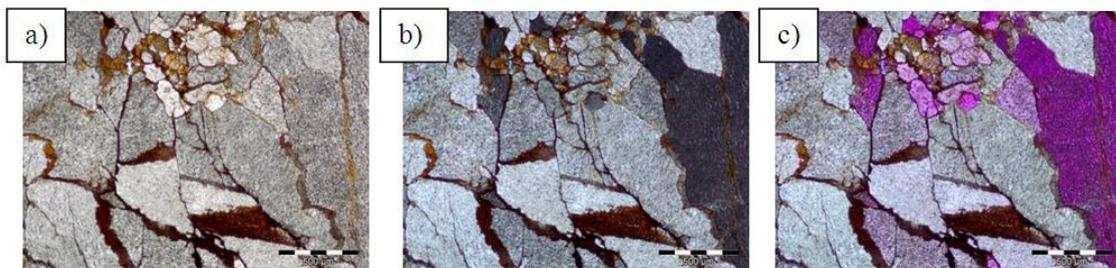


Fig. 3. Characteristic part of the barite aggregate B4 with visible siderite crystals: a) PPL, b) XPL c) XPL with lambda plate (scale bar=500µm).

The analyzed barite B1 had similar mineral composition to barite B2, but instead of siderite and hawleyite it contained fluorite, Fig. 4. The size and texture of SiO_2 crystals in B1 should not influence the possible occurrence of ASR.

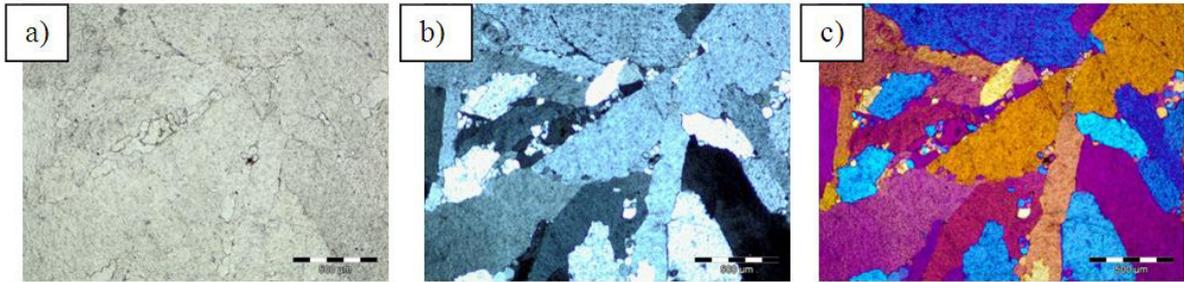


Fig. 4. Characteristic part of the barite aggregate - B1: a) PPL, b) XPL c) XPL with lambda plate (scale bar = 500 µm).

The most interesting observations in relation to ASR were made on thin sections of barite B3, Fig. 5. Except of crystals of barium sulphate and most common form of silica minerals - quartz, also the cristobalite was found. The crystalline, low-density polymorphous form of SiO_2 such as cristobalite is visible on thin sections; it looks like very small (below 1 mm, but bigger than 0.002 mm, Jacobsen [8] black and white particles. Also in barite B3 the presence of microcrystalline quartz were observed, which was characterised by its crystals size equal to appr. 0.004 - 0.062 mm. The reactivity of silica increases with decreased crystal size. Therefore, especially the rocks containing micro-crystalline and crypto-crystalline quartz are potentially reactive in concrete. The observations made on barite B3 suggest that this aggregate could be prone to ASR.

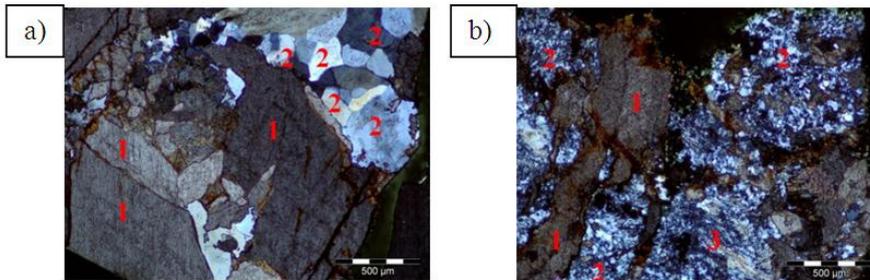


Fig. 5. Characteristic part of the barite aggregate – B3, XPL with visible: a) barite (1) and quartz (2) grains, b) barite, quartz and cristobalite (3), (scale bar = 500µm).

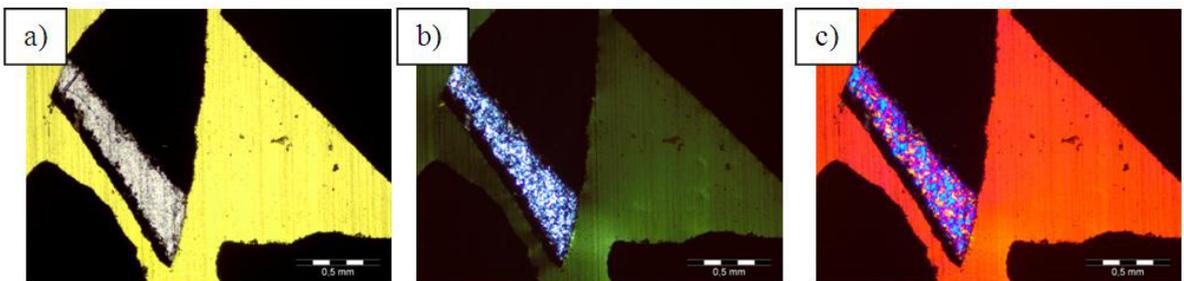


Fig. 6. Hematite aggregate – H (black colour) with visible quartz crystals: a) PPL, b) XPL c) XPL with lambda plate, (scale bar = 500µm).

Magnetite and hematite aggregates contained mostly iron compounds, which are opaque in the thin sections

analysis. In magnetite aggregate some signs of deleterious SiO_2 content have been found. In hematite small size crystals of SiO_2 have been found, Figs. 6 and 7. The size of crystals was comprised between 15 and 60 μm , what makes them microcrystalline and are small enough to be visible in microscope. These kinds of SiO_2 crystals are prone to ASR in concrete.

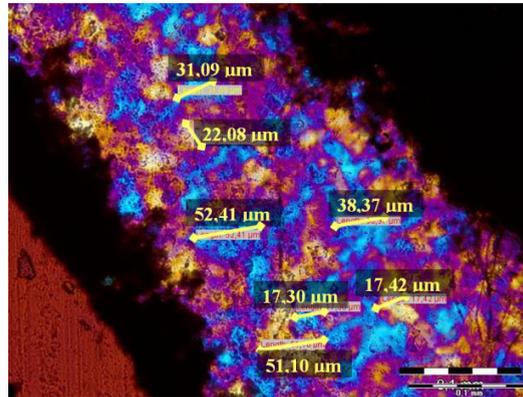


Fig. 7. Hematite aggregate – H with visible quartz crystals size; XPL with lambda plate, (scale bar = 100 μm).

The thin sections analysis on the hematite aggregate has been performed in cross-polarized light with lambda plate, taking profit of the best possible contrast in colors between background (orange) and the grains of hematite which consisted of Fe_2O_3 (black) and SiO_2 (rainbow), Fig. 8. After morphological transformation the automatic image analysis system was able to calculate the contents of quartz in hematite and it was equal to 6% (11.5% according to suppliers data). More advanced analysis is needed to determine the microcrystalline forms of quartz only, which are more dangerous than fine-grained (0.062-1 mm) and medium-grained crystals (1-5 mm) forms.

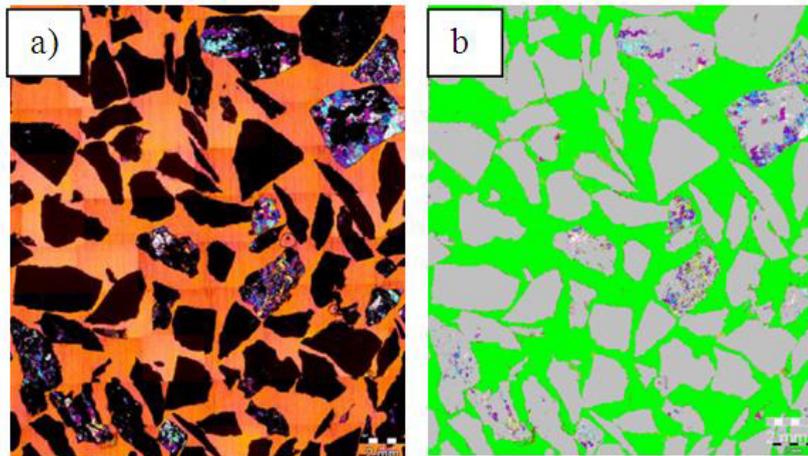


Fig. 8. Hematite aggregate H, a) XPL with lambda plate, b) after morphological transformation (visible SiO_2 content is in “rainbow colors”), (scale bar = 2 mm).

Results of the XRD analysis are presented in Table 3. In all tested barite aggregate, not only barium sulfate was present, but also quartz (SiO_2), what is important because of a possibility of ASR. In barite B3 the cristobalite was found, which is considered as a highly reactive form of quartz causing alkali-silica reaction, Józwiak-Niedźwiedzka et al. [9], Farny and Kosmatka [2], stated that if in an aggregate even a small amount of cristobalite

(about 1%) does exist, the concrete made with this aggregate is prone to cracking due to ASR. Other minerals like hawleyite (CdS), fluorite (CaF_2) and siderite (FeCO_3) were also identified in XRD analysis. The obtained results suggest that barites B2 and B4, although obtained from different mines, had a similar mineral composition, and probably they were related to the same barite deposits.

Table 3. Special aggregates for shielding concrete - main constituents according to XRD method.

Aggregate	Main minerals			
Barite, B1	barite	quartz	fluorite	
	BaSO_4	SiO_2	CaF_2	
Barite, B2	barite	siderite	hawleyite	quartz
	BaSO_4	FeCO_3	CdS	SiO_2
Barite, B3	barite	quartz	crystalite	pringleite
	BaSO_4	SiO_2	SiO_2	$(\text{Ca}_9\text{B}_{26}\text{O}_{34}(\text{OH})_{24}\text{Cl}_4 \cdot 13\text{H}_2\text{O})$
Barite, B4	barite	siderite	hawleyite	quartz
	BaSO_4	FeCO_3	CdS	SiO_2
Magnetite, M	magnetite	magnesioferrite		
	Fe_3O_4	$\text{Mg}(\text{Fe}^{3+})_2\text{O}_4$		
Hematite, H	hematite	quartz		
	Fe_2O_3	SiO_2		

Expansion tests on mortar specimens according to ASTM C1260 revealed significant differences in expansion for different types of aggregates. For hematite aggregate the expansion was 0.31%, for magnetite aggregate – 0.02% and for barites aggregates varied from 0.02% (B4) to 0.10% (B3), Józwiak-Niedźwiedzka et. al [9]. After the expansion test mortar specimens were sectioned and the thin sections were prepared for ASR gel search. The reactive cristobalite, previously found in barite B3, was the reason of the ASR occurrence in the mortar bars. As the evidence of alkali-silica reaction cracking and microcracking occurred in the barite coarse aggregate particles. Cracks were radiating out from the reacting particles into adjacent cement paste in mortars and the presence of alkali-silica gel in air-voids was observed, Fig. 9.

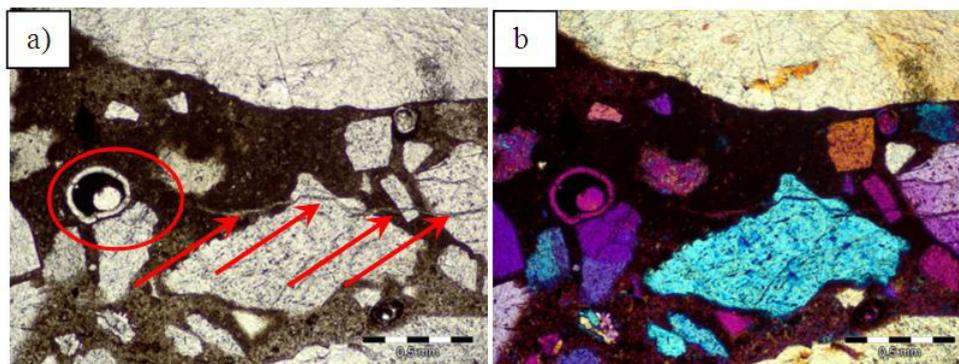


Fig. 9. Cracked mortar with barite B3, alkali-silica gel in air voids.; a) PPL, b) XPL with lambda plate, (scale bar = 500 μm).

4. Conclusions

The results of the thin section analysis showed mineralogical composition of tested aggregates.

In all tested aggregates the siliceous components have been found, but not all of them were associated with potentially deleterious alkali-silica reactivity. The poorly ordered silica is difficult to be characterised and determined by techniques such as X-ray diffraction, because of its low degree of crystallinity, but the analysis

performed on thin sections revealed that different forms of silica were present in aggregates.

One of tested barites - B3 contained cristobalite, which is a reactive form of silica. The performed test allowed to confirm that prognosis – the barite B3 provoked deleterious ASR in mortars. In all other barites and in magnetite the size of SiO₂ crystals can be classified as not threatened with alkali-silica reaction.

The size of SiO₂ crystals in hematite was determined using image analysis. The silica crystals were classified as microcrystalline, so the hematite should be considered as potentially reactive. It is however difficult to know how much potentially reactive silica must be contained in a rock in order to be on the unsafe side. This depends on the type of aggregate: is it pure silica or only containing small amount of silica.

The quantitative analysis of SiO₂ content in hematite has been done and it showed that quartz represents 6% of hematite aggregate, which is less than obtained from supplier's data.

The thin section analysis revealed that the same aggregates, as barite, but from other quarry differs each other in mineral composition. That is why, it is not enough to consider only the type of a rock as a criterion for its potential for reactivity, but its mineralogical composition has to be considered also. The thin section analysis gives the possibility to verify the aggregates and rocks whether they contain silica in one of its forms that may be potentially alkali reactive.

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