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QUANTIFYING PYRITE AND MICA CONTENTS WITHIN CONCRETE AGGREGATES USING PETROGRAPHY AND WHOLE-ROCK GEOCHEMISTRY

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Abstract

River aggregates are commonly used in concrete materials, which may contain harmful minerals, causing severe deterioration by oxidation and reduction of strength with incorporation in excess amounts. Quantification of some harmful minerals, e.g. pyrite and mica, may involve highly laborious and time-consuming processes. Here we suggest an approach for quantification of minerals using thin-section petrography and whole-rock geochemistry. Systematic measurements giving quantitative percentage of minerals obtained from petrography were correlated with CIPW norm mineralogy derived from whole-rock geochemistry. Our results showed that combination of petrography and geochemistry can be considered as a useful approach for determination of harmful minerals in an efficient way.

Keywords: concrete, pyrite, sulphur, mica, petrography, whole-rock geochemistry, CIPW norm

1. Introduction

Sand and gravel are commonly mined for aggregates from river deposits during dam construction, which creates an enormous demand for large reserves of concrete material [1]. River aggregates, which form the natural source of sand and gravel, are derived from diverse sources that contain heterogeneous rock types within river beds. Use of river aggregates in concrete should be considered with caution as some natural minerals forming the aggregates may lead to quality decrease or deterioration of concrete by various types of chemical reactions [2,3,4]. Some natural minerals, pyrite and mica, were reported as harmful minerals within concrete aggregates [5]. The oxidation of pyrite generates a sulphuric acid that causes rusting and corrosion of iron and steel used in construction and is responsible for expansion of concrete [3,6] while mica reduces the strength of concrete up to 15% with wt. 5% mica. Here we report a case study of thin-section petrography and whole-rock geochemistry of a number of concrete samples from Devoll river alluvium and massive limestone, which allow us to quantify the harmful minerals in an efficient way.

2. Methodology

Petrographic studies were carried out on five concrete samples that were mixed with river sediments and massive limestone aggregates at variable proportions (Fig. 1a,b). Devoll alluvium material is located on 6.5 km upstream of Banja dam body in Elbasan and source of limestones is Vellezerit HYSA quarry in Mollas, Albania. Proportions and concrete classes were given in Table 1. Each prismatic sample, which has dimensions of 15×15×7 cm, was cut into two volumetrically equal parts using diamond saw. One part was completely crushed into mm-size fragments, and then powdered for whole rock geochemical analysis in order to

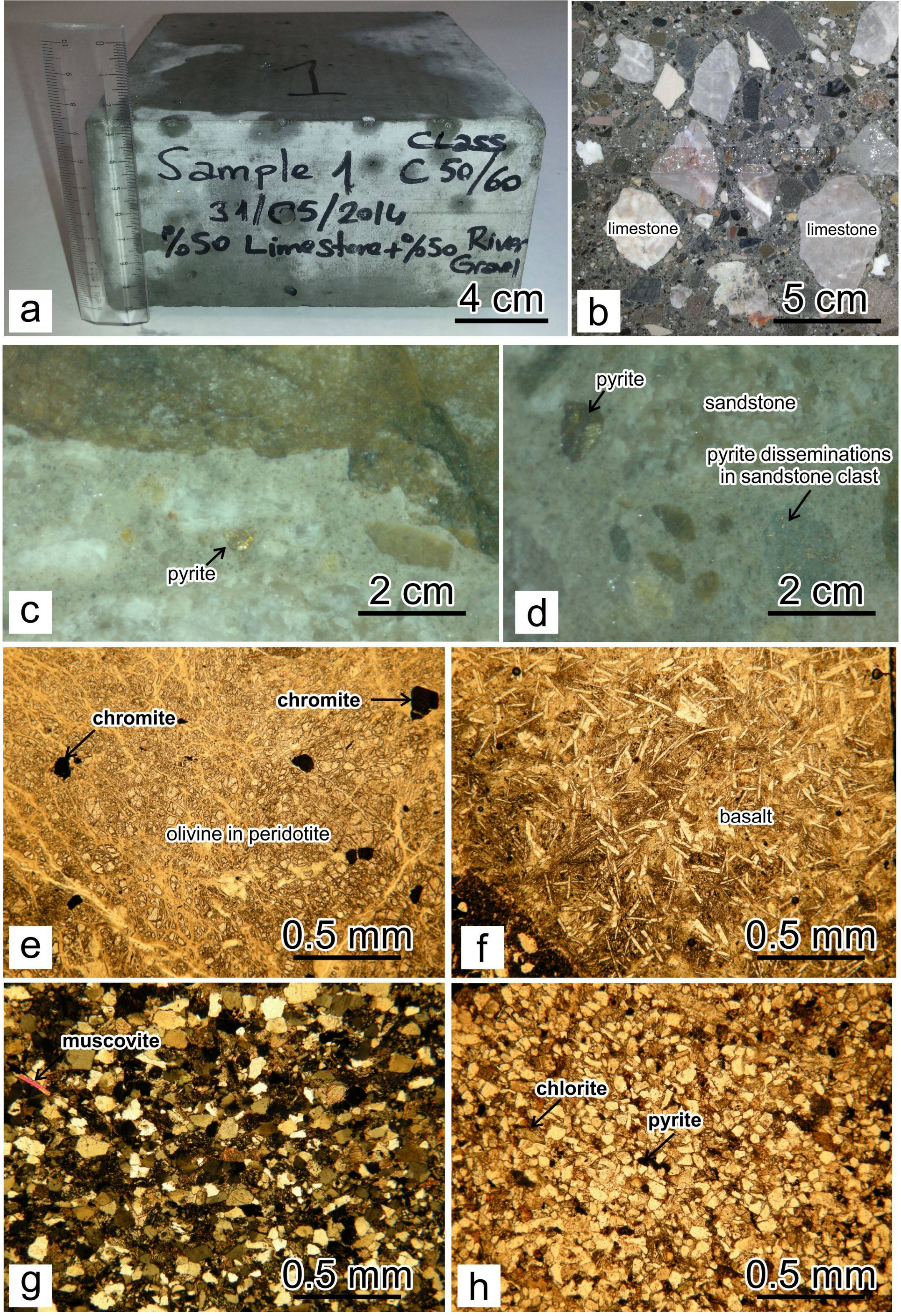

Figure 1: General petrographic characteristics of the concrete samples. a) prismatic concrete sample for petrography and geochemical analysis. c) clast distribution in concrete sample. c) large single euhedral pyrite crystals observed on stereomicroscope. d) pyrite crystal in sandstone clast under stereomicroscope. e) general appearance of olivine crystals together with chromite in peridotite clast. Plane polarized light. f) basalt clast in the concrete sample without any mafic mineral. Plane polarized light. g) relatively large muscovite (mica) crystals within sandstones. Crossed polarized light. h) pyrite and chlorite grains in sandstone clasts. Plane polarized light.

Table 1. General characteristics of concrete samples.

Sample no	concrete class	clast size of river material (mm)	percentage of river material	percentage of limestone aggregate
S-1	C50/60	12-32	50	50
S-2	C50/60	12-32	70	30
S-3	C30/37	12-32	50	50
S-4	C50/60	12-32	30	70
S-5	C50/60	12-32	100	-

measure major oxide and trace element content together with native sulphur content. Rock splits after jaw crushing were selected by quarter method for powdering. Other part has been cut into five slabs for thin section preparation. Slabs were investigated by stereomicroscope in order to determine pyrite grains (Fig. 1 c,d). A total of five thin sections from each sample were prepared at the Middle East Technical University for petrographic determinations and slabs for thin sections were grinded into 30 µm thickness. Slabs prepared for petrographic analysis were chosen to represent overall characteristics of each concrete sample. Petrographic determinations were carried out to define quantitative percentage of rock fragments together with mica and pyrite content in two dimensions that cover a thin section area of 3x2 cm. Nikon 50iPOL light polarised microscope was used for petrographic determinations.

A total of 50 gr powdered sample has been submitted to the ACME Analytical Laboratories in Vancouver, Canada. Iron ore analysis by LF730 analytical method procedure of the laboratory were completed by fused disc X-Ray Fluorescence Spectrometry using the ISO-9516 guideline, which provides robust and precise data for critical mineralogical information about Fe-bearing phases in the sample. Moisture and loss on ignition (LOI) are determined separately at 105^{o}C and 1000^{o}C. Dried ores are mixed with a lithium metaborate/tetraborate and sodium nitrate flux in a humidity controlled environment to eliminate variability caused by water absorption, followed by fusion and casting into glass discs. Fused discs are entirely homogeneous and eliminate matrix and grain size variability. The data produced were verified with a full spectrum of iron ore specific certified reference material.

3. Results and discussion

3.1. Petrographic characteristics of aggregates

River sediments consist of ophiolitic rocks, limestone, sandstone and minor metamorphic and volcanic fragments and are mainly derived from ophiolitic source (Fig. 1e,f). Ophiolitic rocks are characterised by mafic and ultramafic rocks which are formed by dunite, peridotite, gabbro and basalts. Dunite is most common clast type among ophiolitic rocks and is entirely composed of anhedral olivine crystals that were locally strongly iddingsitized and serpentinized. Peridotites are made up of olivine and pyroxene minerals with minor chromite crystals. Pyroxenes within the peridotites are locally altered to tremolite/actinolite and chlorite minerals along fractures and rims. Gabbro clasts are characterized by their ophitic texture and mainly comprise plagioclase and pyroxene crystals. Basalts have similar mineralogical composition to those of gabbros and display typical microlitic and ophitic texture. Dunites and peridotites include minor chromite and magnetite crystals as opaque phase. Ophiolitic rocks are lacking of significant hydrothermal alteration, causing crystallisation of hydrothermal pyrite. Chromite, magnetite and limonite are other common opaque minerals within ultramafic and mafic rocks. Mica minerals are absent in these rocks. Pyrites can be easily distinguished by their iron oxide rim while chromite can be identified by its unaltered appearance within olivines. Metamorphic rock fragments are characterized by polycrystalline deformed quartz grains.

Sandstones are made up of well-sorted quartz, feldspar, mica and minor opaque minerals (Fig. 1g,h). Micas within sandstones comprise muscovite, sericite, biotite and chlorite. Feldspars are commonly altered to sericite and clay minerals. Chlorites appear to have been derived from alteration of biotites. Limestones within river sediments are cream coloured, rounded clasts and consist entirely of microcrystalline calcite. Limestones do not display any type of alteration. Highest proportion of mica and pyrite occurs within sandstones. Each sandstone clast may contain up to 30% mica and pyrite.

Petrographic analysis of clasts indicates that distribution of rock types in the river sediments is significantly heterogeneous (Table 2). It can also be noted that proportion of sandstone clasts clearly increases the mica and pyrite contents in the samples. It can also be noted that the mica and pyrite contents in the samples clearly increase with the increasing proportion of sandstone clasts.

3.2. Geochemistry of concrete samples

Whole-rock major and trace element geochemical data obtained from concrete samples were presented in Table 3. Whole-rock geochemistry reflects the addition of various rock components as defined by relatively low SiO_2, Al_2O_3, Fe_2O_3, MgO, K_2O, MnO, TiO_2, P_2O_5 and Cr_2O3 and high CaO content in the concrete samples S-2 and S-5. This can be correlated with abundance of massive limestone aggregates (Tables 3, 4). Concrete samples have high SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO values while trace element content is significantly low. Native sulphur contents of the concrete samples are close to each other, ranging from 0.15 to 0.17 wt%. High LOI values indicate that increase in LOI can be correlated with the increasing hydrous and/or volatile content together with limestone abundance.

Whole-rock geochemical analyses were carried out in order to calculate mineral content using CIPW norm and oxides (e.g., weight oxides) of any rock can be used as a powerful tool to quantify an idealized mineralogy (i.e. normative mineralogy) of a rock. For background knowledge regarding the calculation of normative mineralogy, readers are referred to Best (1982) Kelsey (1965), Middlemost (1986) and Pruseth (2009) [7,8,9,10]. Norm calculations of chemical analysis obtained from concrete samples were correlated with abundance of minerals defined by petrographic analysis. CIPW mineral norm calculations were presented in Table 5. It can also be noted that normative calculation can only be applied specific minerals for concrete samples as mica minerals have complex mineral formulae that can solely be calculated from natural rock samples. Therefore, norm calculations were done for olivine, feldspar, larnite ($CaO.SiO_3$), ilmenite, apatite and pyrite minerals. Larnite corresponds to belite in concrete, which is one of the main compounds of modern Portland cement. Calcite and silica reactions at high temperatures led to crystallization of larnite, which was also calculated using normative mineralogy. Larnite content can be correlated with those of carbonates defined in petrographic analysis.

Table 2. Clast and mineral constituents of the concrete samples.

	Rock fragments (%)					Mineral content (%)							
Sample	**Sandstone**	**Limestone**	**Ophiolitic rocks**	**Volcanic fragments**	**Metamorphic fragments**	**Olivine serpentinite chrominte**	**Pyroxene**	**Feldspar**	**Quartz**	**Amphibole**	**Carbonate**	**Mica minerals**	**Pyrite**
S-1a	35	20	35	10		23	17	9	30		20	1.1	0.9
S-1b	65	30	4		1	4			44		49	0.9	0.4
S-1c	5	85	5	5		5	3	4	3		85	0.2	0.1
S-1d	40	50	6		4	6			30		62	1.3	0.7
S-1e	15	80	4	1		3	1	5	10		80	0.5	0.2
Average	**32**	**53**	**11**	**5**	**3**	**8**	**7**	**6**	**23**		**59**	**0.8**	**0.5**
S-2a	4	55	40	1	1	25	8	7	4		56	0.1	0.1
S-2b	35	50	15			15			21		63	0.5	0.5
S-2c	15	35	50			43	8		7		42	0.5	0.5
S-2d	35	25	40			20	20		20		39	0.5	1.0
Average	**22**	**41**	**36**	**1**	**1**	**26**	**12**	**7**	**13**		**50**	**0.4**	**0.5**
S-3a	10	85	5			5		5	5		85	0.5	0.2
S-3b	57	33	10			10			36		50	2.3	1.8
S-3c	30	55	5		10	5		4	19	1	70	0.5	0.5
S-3d	45	50	5			5			33		60	1.7	0.5
S-3e	10	28	60		2	60			8		32	0.4	0.1
Average	**30**	**50**	**17**		**6**	**17**		**4**	**20**	**1**	**59**	**1.1**	**0.6**
S-4a	45	40	13		2	13			22		63	0.6	0.9
S-4b	26	20	50	3	1	20	12	17	14	3	34	0.5	
S-4c	10	70	19	1		19	1	1	5		74	0.1	0.1
S-4d	20	70	10			7	3	3	14		72	0.8	0.2
S-4e	20	70	10			7	3	3	16		70	0.8	0.2
Average	**24**	**54**	**20**	**2**	**2**	**13**	**5**	**6**	**14**	**3**	**63**	**0.6**	**0.4**
S-5a	40	55	4		1	2	2	9	31		55	1.2	1.2
S-5b	75	10	15			10	5	15	52		15	1.0	2.3
S-5c	39	49	10	1	1	7	3	8	23		58	0.4	0.1
S-5d	35	40	25			25		5	23		45	1.4	0.3
S-5e	30	35	20	15		20	7	7	16		49	0.9	0.8
Average	**44**	**38**	**15**	**8**	**1**	**13**	**4**	**9**	**29**		**44**	**1.0**	**0.9**

Table 4. Major and trace element contents of the concrete samples

Sample	S-1	S-2	S-3	S-4	S-5	GIOP-55*	FER-1(D)*	NIST693(D)*
SiO_2	28.73	30.13	24.59	23.66	34.12	4.09	16.85	3.89
Al_2O_3	2.94	2.89	2.82	2.78	3.74	2.2	0.5	1.05
Fe_2O_3	2.96	3.71	2.81	2.5	3.39	90.47	75.5	93.99
CaO	33.21	29.12	35.58	38.09	29.71	0.05	3.3	0.02
MgO	9	12.93	8.57	7.16	9.11	0.05	0.31	<0.01
K_2O	0.38	0.36	0.31	0.34	0.48	0.02	0.01	<0.01
MnO	0.09	0.12	0.09	0.08	0.11	0.09	0.22	0.08
TiO_2	0.19	0.18	0.17	0.17	0.22	0.1	0.03	0.03
P_2O_5	0.03	0.03	0.03	0.03	0.04	0.17	2.38	0.12
Cr_2O_3	0.124	0.157	0.108	0.119	0.134	0.008	<0.004	0.008
Co	0.008	0.008	0.011	0.007	0.01	<0.001	<0.001	<0.001
Cu	0.008	0.008	0.009	0.008	0.015	0.006	0.012	0.004
Ni	0.049	0.068	0.045	0.036	0.047	0.002	<0.001	<0.001
S	0.206	0.172	0.153	0.23	0.274	0.017	0.263	<0.001
Sr	0.017	0.025	0.018	0.022	0.025	<0.002	0.009	<0.002
Zn	0.003	0.003	0.004	0.003	0.003	0.002	0.35	<0.001
LOI	23.03	21.33	25	24.77	18.51	3.33	-0.58	1.94
SUM	100.99	101.24	100.35	100.01	99.97	100.62	100.02	101.16

* Reference materials provided by laboratory.
Major and trace elements are in wt. %; LOI: loss on ignition

Table 5. CIPW normative mineral content (in wt. %) of concrete samples based on whole-rock geochemistry.

Sample no	Chemical formula	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Plagioclase	$NaAlSi_3O_8$–$CaAl_2Si_2O_8$	8.87	8.63	9.05	8.88	10.33
Olivine	$(Mg, Fe)_2SiO_4$	25.02	34.33	24.76	20.75	15.35
Larnite	$2CaO.SiO_2$	62.78	53.33	69.83	75.11	41.97
Ilmenite	$FeTiO_3$	0.47	0.44	0.44	0.44	0.51
Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$	0.09	0.09	0.09	0.09	0.12
Pyrite	FeS_2	0.57	0.47	0.42	0.66	0.72

The elements sulfur and iron is major components of pyrite and pyrite content were calculated using native S and FeO in the concrete samples. Calculation is based on the formula weight of pyrite as molecular weight (FeO) + atomic weight (S) × 2 (Table 4). These results show that weight percentage of pyrite based on norm calculation ranges from 0.42 to 0.72 wt %.

3.3. Correlation of petrographic and whole-rock geochemical data

Mineral content estimated by petrographic analysis appears consistent with abundance of minerals calculated using CIPW norm. Especially, larnite, feldspar and pyrite contents obtained from norm calculations are fairly consistent with values estimated by petrographic analysis. Larnite in the concrete samples are very common up to 75 wt%, which is a result of concrete reaction. Larnite content also increases with addition of massive limestone aggregates.

Provided petrographic and geochemical analyses show that all samples contain mica and pyrite less than 2%. Sandstones include much of pyrite and mica, therefore addition of sandstone into concrete material will significantly increase the total pyrite and mica content in the concrete samples. Pyrite and mica percentage can be lowered by incorporation of massive limestone aggregates, which have no pyrite and mica. Ophiolitic rocks and limestones have neglectable amount of pyrite and mica (e.g. chlorite) contents and are suitable material for reduction of mica and pyrite percentage in the bulk sample. CIPW norm calculation is particularly useful for quantification of pyrite in the concrete sample as sulphur percentage in whole-rock geochemical analysis was completely allocated to pyrite content due to absence of other sulphur-bearing mineral phases.

Ilmenite ($FeTiO_2$) and apatite [$Ca_5(PO_4)_3(F, Cl, OH)$] minerals as accessory phases were not determined in petrographic analyses while CIPW norm calculations also indicate the presence of ilmenite and apatite in trace amounts in the concrete sample. In norm calculations elements Ti and P were completely allocated to the mineral formulas of ilmenite and apatite, respectively. Therefore, we suggest that CIPW norm calculations can also be very suitable to define some minerals, which cannot be observed in thin-section petrography.

4. Conclusions

Combined petrographic and geochemical analytical methods can be used as tool to quantify the mineral contents of natural rock aggregates. These methods can be used as basic approach to determine the approximate mineral composition of aggregates within concrete samples. The accuracy of results obtained by thin-section petrography and whole-rock geochemical analysis is constrained by the number of samples analysed and source rock composition of river sediments. Therefore, each case will need to be considered on its own merits for quantification of useful and harmful minerals within concrete aggregates.

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