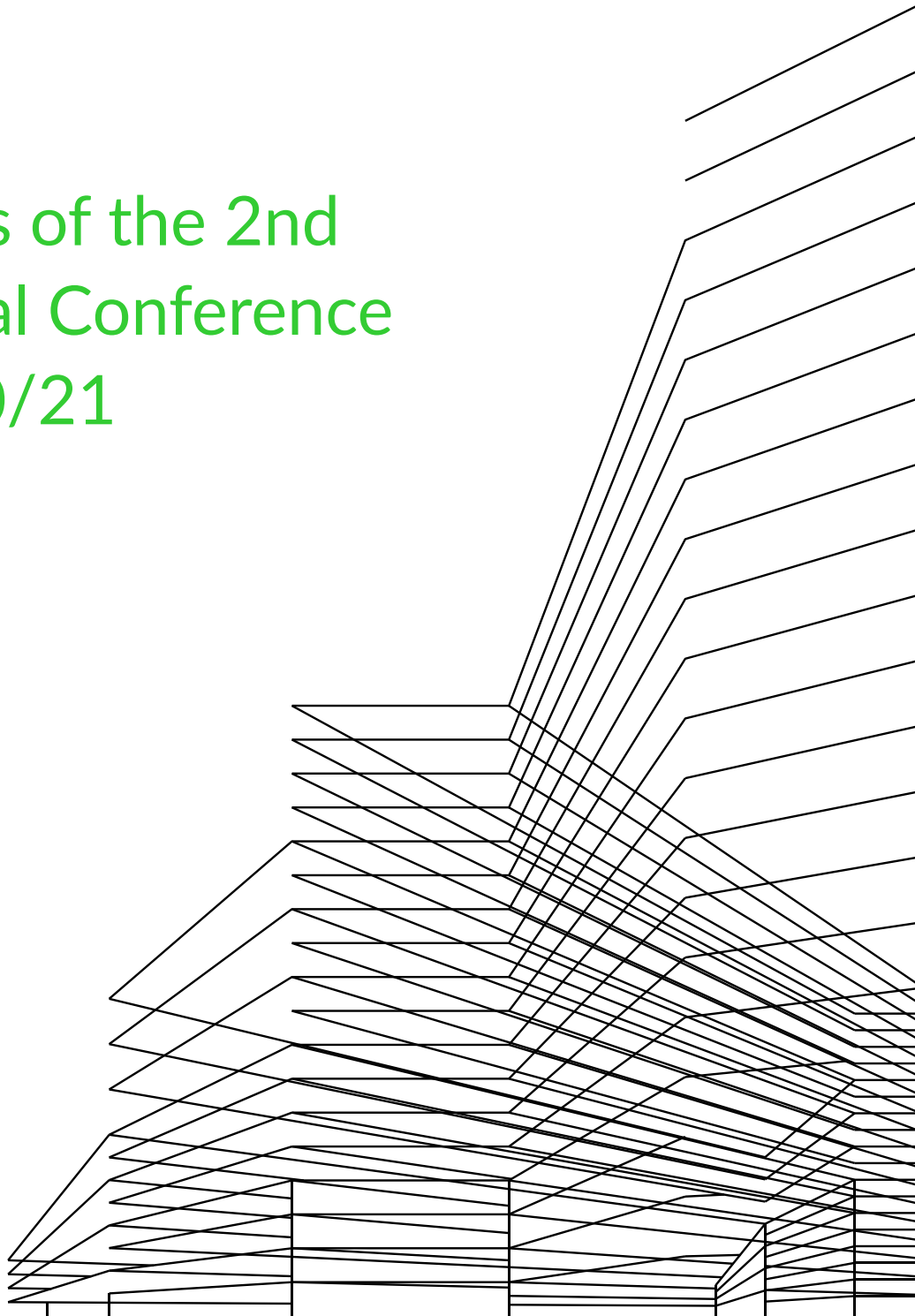
CoMS_
2020/21

Construction Materials for a Sustainable Future

Proceedings of the 2nd International Conference CoMS 2020/21

Volume 1



Slovenian National
Building and Civil
Engineering Institute,
Ljubljana, 2020

Conference CoMS_2020/21, 2nd International Conference on Construction Materials for a Sustainable Future
Editors Aljoša Šajna, Andraž Legat, Sabina Jordan, Petra Horvat, Ema Kemperle, Sabina Dolenec, Metka Ljubešek, Matej Michelizza
Design Eksit ADV, d.o.o.
Published by Slovenian National Building and Civil Engineering Institute (ZAG), Ljubljana, 2020
Price Free copie

First electronic edition

Available at http://www.zag.si/dl/coms2020-21-proceedings.pdf

http://www.zag.si

ISBN 978-961-94071-8-9 (pdf)

CIP - Kataložni zapis o publikaciji pripravili v Narodni in univerzitetni knjižnici v Ljubljani
COBISS.SI-ID=44042499
ISBN 978-961-94071-8-9 (pdf)

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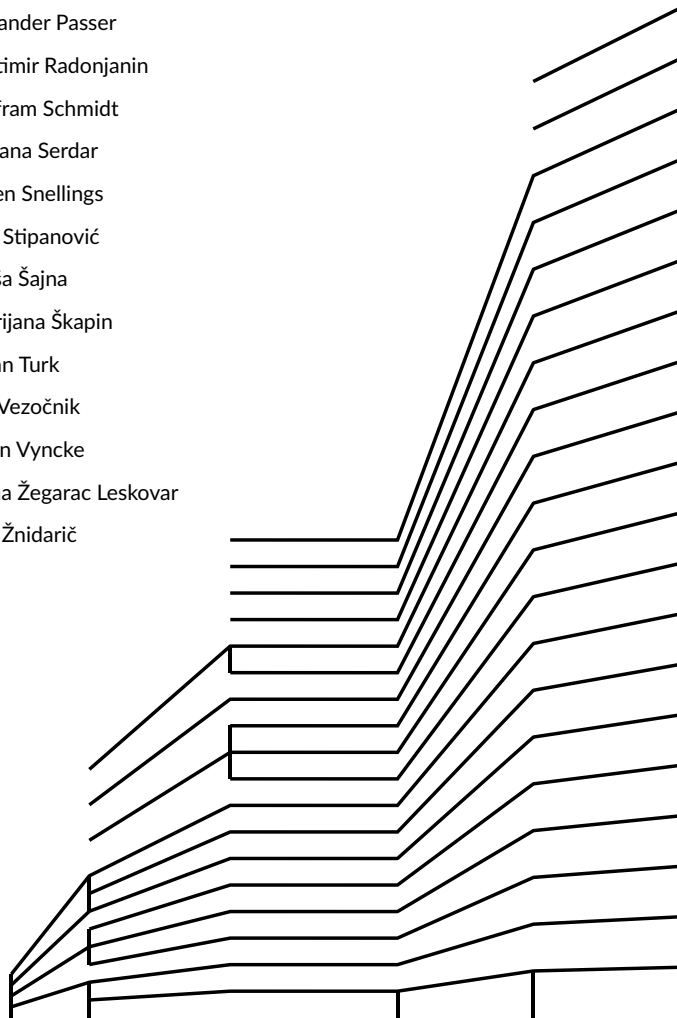

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EFFECT OF ACCELERATED CARBONATION ON THE EFFICIENCY OF IMMOBILIZATION OF Cs IN THE ALKALI-ACTIVATED BLAST FURNACE SLAG

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SUMMARY: In this paper the effect of accelerated carbonation process on the effectiveness of immobilization of cesium (simulated radioactive and toxic waste) in the alkali-activated blast furnace slag (AABFS) matrix was studied. Blast furnace slag (BFS) was contaminated with 2% and 5% Cs (with respect to the dry BFS mass) and alkali-activated with sodium silicate solution, while the AABFS samples were cured sealed in plastic envelopes for 24 h at 95°C. First series of AABFS samples were exposed to accelerated carbonation (open curing), while the second (reference) series of AABFS samples left to aging (also sealed) at room temperature until testing. Thereafter AABFS samples were subjected to a short-term (five-day) leaching tests according to the ANSI/ANS-16.1-2003 standard. The strength of AABFS mortars were tested according to the SRPS EN 196-1 standard, while the carbonation was confirmed by phenolphthalein test and SEM analysis. The diffusion coefficient (D) and non-dimensional leachability index (L) of cesium leached from AABFS were calculated according to the ANSI/ANS-16.1–2003 standard. A correlation between the accelerated carbonation process and the effectiveness of immobilization of cesium in AABFS was established.

Keywords: Carbonation; Immobilization; Cesium; Simulated radioactive waste; Alkali-activated binders; Blast furnace slag.

1 INTRODUCTION

Alkali-activated binders (AABs), as a promising alternative to traditional Portland cement binders in the concept of sustainable development, have drawn significant public attention around the world in the past several decades. AABs have not only been frequently studied by the researchers but also applied in various industries, including the construction industry. Among various possible applications, the immobilization of hazardous, toxic, and nuclear wastes with AABs presents quite an interesting option, which might contribute significantly to the environmental protection [1].

Blast furnace slag (BFS) is a by-product from pig iron production and it is frequently used as supplementary cementitious material in cement and concrete industry. On the other hand, alkali-activated blast furnace slag (AABFS) seem to be a better option than traditional Portland cement binders for immobilization of hazardous, toxic, and nuclear wastes due to better physical and mechanical properties of AABFS, as well as better resistance to different corrosive environments [2].

Cesium is considered as one of the most difficult radionuclide to immobilize due to its weak bonding and high mobility within many common binder matrices. Generally, strength and leaching testing are considered to provide the most significant information regarding the efficiency of toxic and radioactive waste immobilization, and so are widely used to determine the influence of immobilized species on the properties of AABs [3].

In this paper, the impact of accelerated carbonation process on leaching and strength of AABFS doped with 2% and 5% cesium (i.e., a solidified simulated radioactive waste) was investigated. A short-term (5 days) leaching procedure was performed according to the ANSI/ANS-16.1-2003 standard [4].

2 EXPERIMENTAL

2.1 Materials

In this work, ground granulated blast furnace slag (BFS) from pig iron production at the facility "Železara Smederevo" (Serbia) was used as a solid precursor for the synthesis of AABFS. Sodium silicate solution was used as an alkali activator, while cesium chloride was used as the Cs source. This paper is a continuation of our previously published work [3] and more details regarding the properties of all materials used and experimental procedures are given there.

2.2 Paste preparation

The AABFS pastes were prepared by mixing ground granulated BFS, sodium silicate solution, and water or cesium chloride solution (in the case of AABFS doped with Cs). The amount of Na_2O was 4% in all cases, and the doping level of Cs was either 2.0% or 5.0% with respect to the total mass of BFS. The mix proportions of AABFS pastes, as well as their setting times according to the EN 196-3 standard [5] are given in Table 1. The AABFS paste was mixed for two minutes, then cast into a cylindrical plastic mold (ø 60 × 10 mm), after which the air bubbles were removed using a vibrating table. The AABFS pastes were cured covered with plastic sheet for 24 h at 95 °C, and then either rapidly carbonated in a chamber at room temperature or cured covered also at room temperature until testing. For SEM analysis, selected fragments of the AABFS paste samples were immersed in isopropyl alcohol for 24 h and and then dried at 50 ºC for 2 h. Prior to the SEM analysis the samples were Au-coated.

Table 1: AABFS paste composition and setting time

Sample	BFS mass (g)	Sodium silicate mass (g)	Added water mass (g)	CsCl mass (g)	Water/ binder ratio	Setting time (min)	
						Initial	Final
AABFS	675	162.15	60	0.0	0.205 ± 0.05	15	30
AABFS + 2% Cs				17.1		40	60
AABFS + 5% Cs				42.75		60	80

2.3 Mortar preparation

Mortars of AABFS were prepared by adding the activator solution of specified concentration to water (containing CsCl for doped samples) and then mixing this solution with the BFS and standard sand (BFS/sand ratio was 1:3) in accordance with the EN 196–1 standard [6]. Mortars were homogenized in an automatic mixer for 3 min and cast into triplicate mortar prisms (40 × 40 × 160 mm) on a vibrating table. The AABFS mortars were cured under the same conditions as the AABFS pastes.

2.4 Accelerated carbonation

AABFS paste and mortar samples were subjected to the accelerated carbonation according to the EN 13295: 2004 standard [7] in the carbonation chamber (type MEMMERT ICH 260C, Figure 1). Prior to exposure to high CO_2 concentration, the samples were pre-conditioned in the laboratory for a period of 14 days at 21 ± 2°C and 60 ± 10% relative humidity, until they reached a constant mass. Thereafter, the samples were placed in a carbonation chamber, and exposed to the CO_2 concentration of 1.0%, also at RH 60 ± 10% and 21 ± 2°C, for a period of 56 days. After 56 days of open curing in a chamber, samples were broken using three point bending test method. The carbonation depth was examined by phenolphthalein test on a cross section of mortar prisms, while the formation of carbonate phases in the pores of AABFS matrix was confirmed by the SEM analysis (Figure 2).

Figure 1: Accelerated carbonation chamber

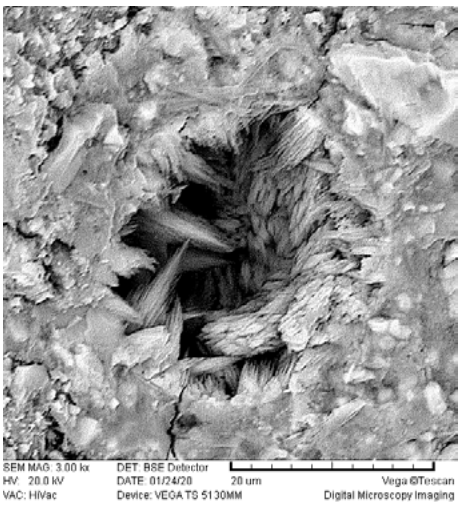

Figure 2: Carbonation identification (phenolphthalein test – left, SEM analysis – right)

2.5 Mortar strength

The strengths of all AABFS mortars were determined according to the EN 196-1 (2008) standard [6], using a Compression testing machine (Matest, Italy).

2.6 Leaching tests

Leaching of different elements (Si, Al, Ca, Mg, Na, K, Fe, and Cs) from hardened (both reference and rapidly carbonated) AABFS pastes was determined according to the ANSI/ANS-16.1-2003 standard procedure. This test is a semi-dynamic leach experiment that consists of submerging a monolithic sample with a fixed geometry, into deionized water at a fixed liquid-volume to solid-geometric surface area ratio, and replacing all of the leachate at given time intervals. The standard leaching test was performed without any stirring within a period of 5 days, where the leachate was completely replaced by fresh leachant after cumulative leach times of 2, 7, 24, 48, 72, 96, and 120 hours. An inductively coupled plasma optical emission spectrometer (ICP–OES, Avio 200, Perkin Elmer, USA) was used to determine the concentrations of leached elements present in the leachate.

3 RESULTS AND DISCUSSION

3.1 Mortar strength

The results of AABFS mortar compressive strength testing are given in Table 2.

Table 2: Mortar strength of AABFS after 90 days (with and without Cs added)

Sample type	AABFS	AABFS + 2% Cs	AABFS + 5% Cs
	Compressive strength and standard deviations (MPa)		
Reference (closed cured)	68.4 ± 2.6	74.1 ± 1.1	73.8 ± 2.8
56 days of accelerated carbonation	81.6 ± 1.3	93.6 ± 2.4	91.5 ± 2.2
	Relative compressive strength *(with respect to its counterpart)*		
Reference (closed cured)	1.00	1.00	1.00
56 days of accelerated carbonation	1.19	1.26	1.24

The AABFS mortar reference samples achieved compressive strengths of almost 70 MPa after 90 days of closed curing, including initial 24 hours of reaction at 95°C. Doping AABFS with 2% or 5% Cs resulted in a slight increase (5-6 MPa) in mortar compressive strength, probably due to promotion of the dissolution of BFS or some structural reorganization of AABFS gels [3].

After 56 days of accelerated carbonation the compressive strength of ABBFS mortars significantly increased (19-26%), regardless of the level of Cs doping (Table 2). It is obvious that the solution present in the pores of AABFS matrix was significantly carbonated in this process (Figure 2), which resulted in likely reduction of matrix porosity and obvious increase in AABFS mortar strength at the same time.

3.2 Leaching

The incremental leach fractions of alkali metal cations (Cs, Na, and K), as well as the AABFS matrix main building blocks (Ca, Si, and Al), present in the leachate over the period of 120 hours are given in Figures 3 and 4, repectively. The concentrations of Mg and Fe present in the leachate were below the detection limit throughout the whole period of testing, and therefore are not shown.

Significant amounts of leached Na, Si, and K were noticed in the case of the reference AABFS (non-doped with Cs and non-carbonated), while their concentration reached its peak after the first 24 hours of testing (Figures 3c, 3e, and 4c). The fast increase of Na, K, and Si concentrations after the first 24 hours of testing was probably due to the leaching of non-bound or loosely bound ions present in the pore solution at or close to the surface of specimens, which is also known as the surface wash-off phenomenon [8]. Between 48 and 120 hours of testing the migration of ions through the AABFS matrix was diffusion controlled, which resulted in lower leaching rates. Generally, the concentration of alkali metal cations (Na, and K) and Si in the leachates was much higher than the concentration of Ca and Al, which means that C-S-H and/or C-A-S-H gels, usually present in the matured AABFS, are highly resistant to water leaching. The excess of sodium silicate (alkali activator) present in the AABFS was probably the main reason of high concentration of Na and Si present in the leachate, while K originated from BFS itself.

The concentration of Cs leached from the reference (non-carbonated) AABFS samples doped with either 2% Cs or 5% Cs also reached its peak after the first 24 hours of testing (Figure 3a). Similar leaching patterns were also present when other elements of interest were tested (Figures 3c, 3e, and 4c). As in the case of Na, K, and Si leaching, the fast increase of Cs concentrations after the first 24 hours of testing was probably due to the leaching of non-bound or loosely bound Cs ions present in the pore solution at or close to the surface of specimens. As already explained, between 48 and 120 hours of testing the migration of ions through the AABFS matrix was diffusion controlled, which resulted in lower leaching rates. Generally, higher addition of Cs promoted not only leaching of Cs, but of Na and Si as well (Figures 3c and 4c).

After accelerated carbonation (Figures 3b,d,f, and 4b,d,f) the leaching patterns of elements tested were more or less similar to the reference AABFS samples. However, the concentraton of leached elements was somewhat lower, particularly in the case of Cs, Ca, and Si, confirming that accelerated carbonation incresed their resistance to leaching, probably due to reduced AABFS matrix porosity. Indirect evidence for this assumption is significant increase in the strength of AABFS mortars.

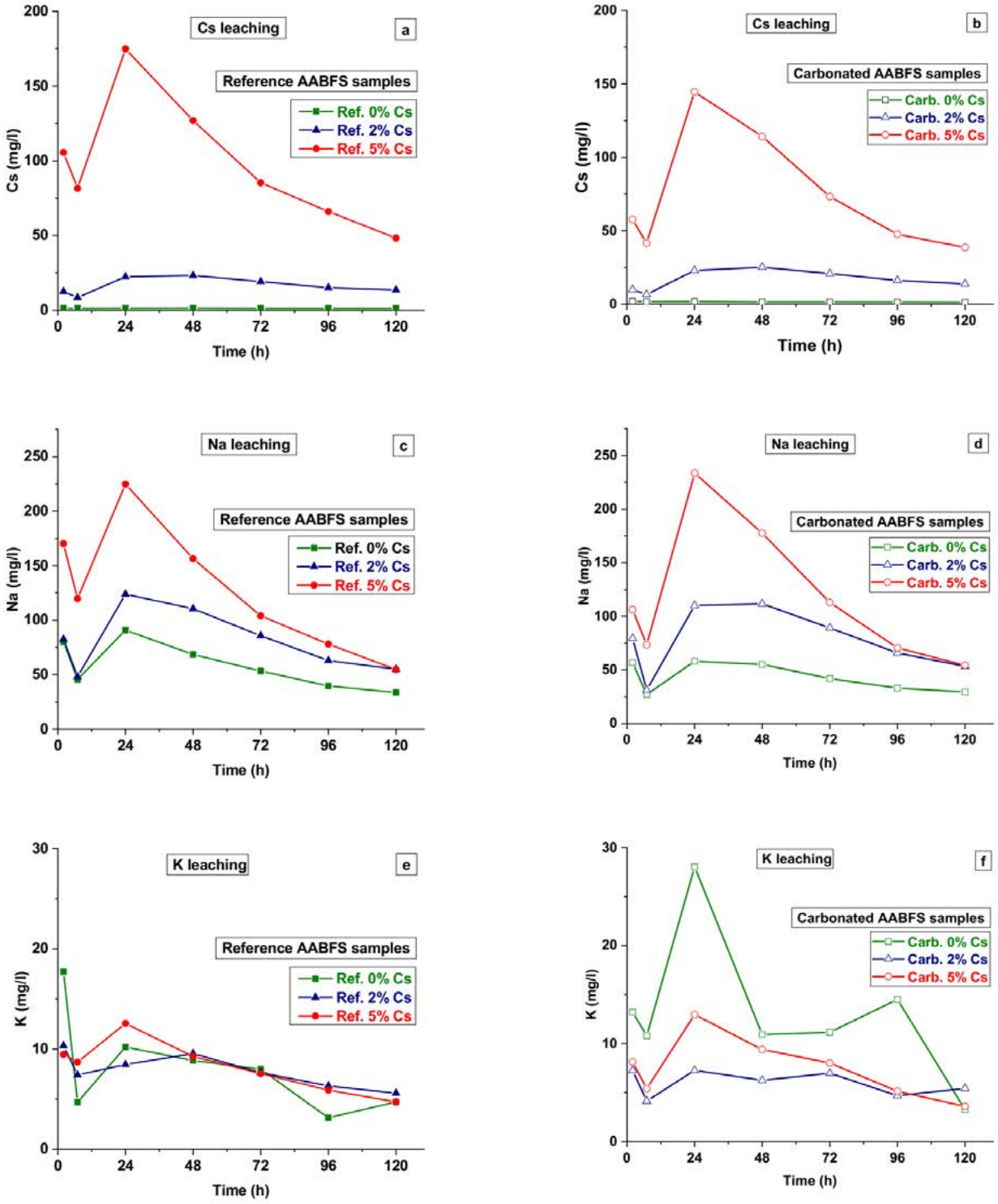

Figure 3: Incremental leaching of Cs, Na, and K from the AABFS matrices up to 120 hours, with and without Cs addition (reference samples - left, carbonated samples – right; analytical uncertainty in each point is approximately 1%)

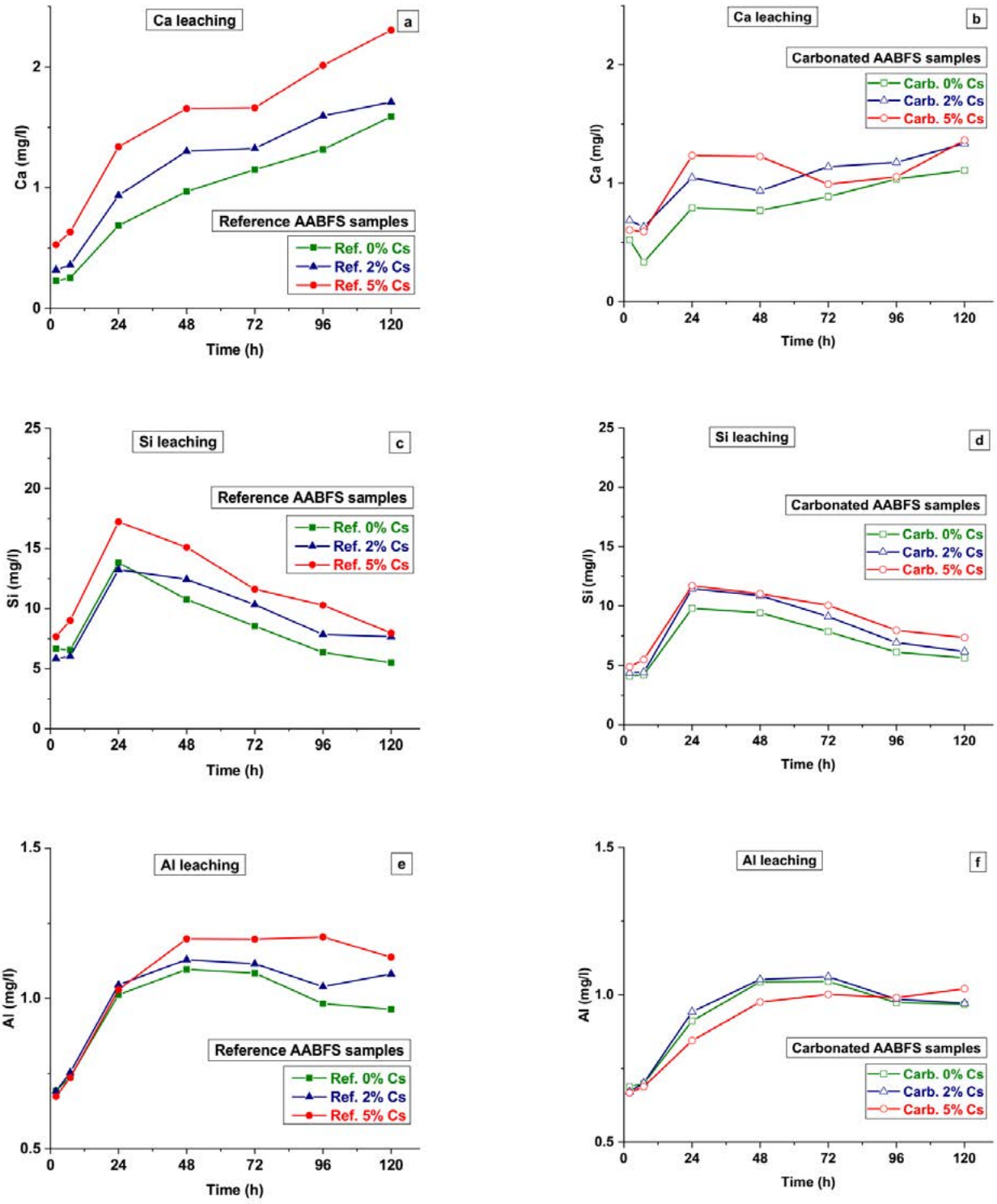

Figure 4: Incremental leaching of Ca, Si, and Al from the AABFS matrices up to 120 hours, with and without Cs addition (reference samples - left, carbonated samples – right; analytical uncertainty in each point is approximately 1%)

3.3 Diffusion coefficient (D) and leachability index (L) of cesium leached from AABFS

The diffusion coefficient (D) and non-dimensional leachability index (L) of cesium leached from AABFS were calculated according to the ANSI/ANS-16.1–2003 standard [4], and given in Figures 5 and 6, respectively.

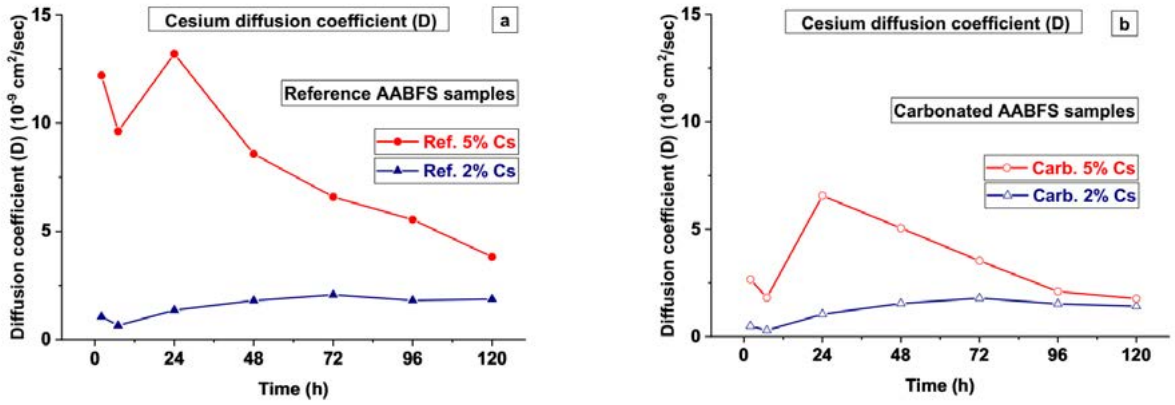

Figure 5: Diffusion coefficient (D) of cesium leached from AABFS versus time (AABFS doped with 2% and 5% Cs; a) reference samples and b) carbonated samples)

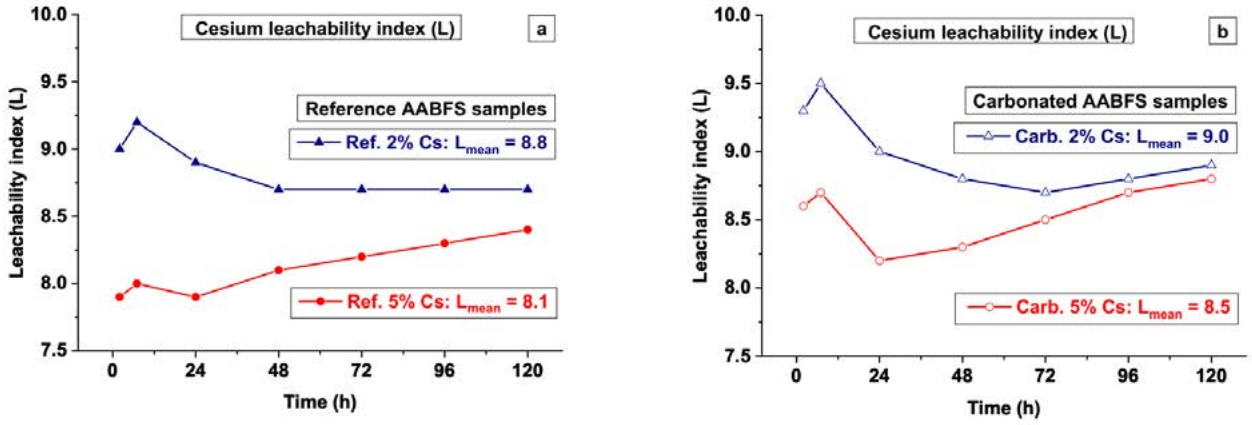

Figure 6: Non-dimensional leachability index (L) of cesium leached from AABFS versus time (AABFS doped with 2% and 5% Cs; a) reference samples and b) carbonated samples)

The leachability index (L) is a parameter that characterizes the leaching resistance of an element of interest. It can be used to estimate the applicability of a certain material or matrix for safe immobilization of hazardous waste, whereby a value of 6 is considered as the threshold for a given matrix to be accepted as adequate for the immobilization of radioactive wastes [9]. As already presented in our previous research [3], the mean leachability index of cesium leached from AABFS doped with 2% and 5% Cs after initial 1 day of closed curing at 95°C exceeded the minimum required value of 6 (Table 3).

Table 3: Mean leachability index (L) of cesium immobilized in AABFS

Addition of Cs	AABFS + Cs		
	After 1 day of closed curing at 95°C [3]	After 1 day of closed curing at 95°C and up to 90 days of closed curing at 21 ± 2°C	After 1 day of closed curing at 95°C and up to 90 days of open curing at 21 ± 2°C (56 days of carbonation)
	Reference samples		Carbonated samples
2%	7.8	8.8	9.0
5%	7.0	8.1	8.5

After prolonged (up to 90 days) curing, the leachability index further increased, exceeding the value of 8 in all cases and even reaching the value of 9 in the case of carbonated AABFS doped with 2% Cs. Therefore, AABFS synthesized under the experimental conditions used in this study can be considered as a potentially efficient matrix for immobilizing cesium from radioactive wastes.

4. CONCLUSIONS

In this paper, the impact of accelerated carbonation process on leaching resistance and strength of AABFS doped with 2% and 5% cesium (i.e., a solidified simulated radioactive waste) was investigated. Accelerated carbonation together with the prolonged curing had positive impact on the effectiveness of immobilization of cesium in AABFS identified by an increase in Leachability index. AABFS synthesized under the experimental conditions used in this study can be considered as a potentially efficient matrix for immobilizing cesium from radioactive wastes.

ACKNOWLEDGEMENTS

This research was financially supported by the NATO SPS programme (project G5402) and the Ministry of Education, Science and Technological Development of the Republic of Serbia (project TR 34026).

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